

Liquid Fuels for Internal Combustion Engines

*A PRACTICAL TREATISE
FOR ENGINEERS & CHEMISTS*

BY

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PREFACE TO SECOND EDITION

THOUGH only two years have elapsed since the first edition left the author's hands, many developments have taken place and numerous researches have been published during this period. It has therefore been necessary to make many additions to the matter of the original edition.

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PREFACE TO FIRST EDITION

THE rapid development of the internal combustion engine during the last twenty years has considerably changed our methods of power production and widened the field of mechanical invention.

A great variety of design is found among internal combustion engines which burn liquid fuels, and as this type is the most recent development of that class of engine, it is not surprising that the scientific study of the fuels used is still incomplete. The earlier investigations of liquid fuels were principally concerned with their use for external combustion. The last few years have, however, seen a change which makes their use for internal combustion the more important. It appears very likely from the trend of modern mechanical invention that, concurrently with the increasing cost of fuel, and with the rapid development of the oil engine and the petrol motor, the employment of liquid fuels for steam raising will entirely give place to their use in the more efficient internal combustion engine. The use of Diesel engines for propelling warships is at present prevented by the insufficiency of experience in building engines of very large size and of low weight in proportion to the power they develop, but these difficulties are by no means insurmountable. The future of the internal combustion turbine is at present a matter for speculation, but there is every possibility that the next twenty years will see great progress made in this direction.

The study of fuel oils is closely connected with

engineering and with chemistry, and a thorough acquaintance with the elements of engineering practice and the basic principles of organic chemistry are essential to an understanding of the subject.

The author has attempted briefly to explain the chemical differences which exist among liquid fuels. Any exhaustive explanation of the chemistry of the compounds present in liquid fuels and the chemical reactions which are involved in their preparation and purification would be outside the scope of this work.

The procedure necessary for the examination and valuation of liquid fuels with a view to their use in internal combustion engines is widely different from the methods employed in the examination of liquid fuels for steam raising purposes, and is much more intricate and delicate. The author, therefore, hopes that this introduction to a somewhat specialised subject may be of assistance to engineers and chemists interested in the internal combustion engine, and perhaps stimulate experimental work in this field.

In the arrangement of Parts I., II., and III. in this book a certain amount of overlapping of material has been unavoidable, and several repetitions of statements have been intentionally made in order to make each part complete in itself as far as possible.

The author wishes to acknowledge his indebtedness to Messrs Baird & Tatlock, of Manchester, for the loan of several blocks for illustrations, to Mr A. J. Wilson for his assistance in the preparation of the drawings and diagrams for this book, and to Messrs Mirrlees, Bickerton & Day, in whose laboratories at Hazel Grove the larger part of the experiments and analyses mentioned in this book have been carried out.

H. M.

20th November 1917.

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INTRODUCTION

BEFORE entering into a study of liquid fuels it is advisable to review the position which this branch occupies in relation to the subject of fuels in general. Fuels are substances which, on combination with air, yield heat in sufficient quantities to make them practically useful as sources of heat. The heat of chemical reactions in which air does not take part is not of sufficient importance to demand their treatment under the subject of fuels.

Fuels naturally divide themselves into three classes: solid, liquid, and gaseous; but this division, like other systems of classification, leaves a few products on the border line between two classes. For example, some fractions obtained by the distillation of petroleum boil at ordinary temperatures (about 15° C.). These might be classified either as very volatile liquids or as easily condensable gases. Similarly, exceedingly viscous asphaltic products are found which might be classified either as solids or liquids. One must recognise that these bodies are on the dividing lines, and may be treated as belonging to either class. For general purposes this classification is satisfactory. Fuels may be also divided into naturally occurring and artificial, but such a division is not necessary or advantageous for the present purpose. A further division may be made from the engineering point of view into fuels for external and fuels for internal combustion. By fuels for external combustion we understand those fuels which are burned under boilers and in furnaces, while

by internal combustion we understand the burning to take place actually in the engine. It is the purpose of this book to deal only with the liquid fuels which are employed in the latter manner.

The study of liquid fuels used for internal combustion necessitates a knowledge of the various types of internal combustion engines in which they are used.

For the present purpose it is most convenient to classify engines using liquid fuel into three types:—

1. Engines fitted with carburetters (generally known as petrol motors).
2. Engines fitted with simple vaporisers (generally known as paraffin motors).
3. Engines fitted with fuel pumps and atomising devices, that is to say, semi-Diesel and Diesel engines.

As the term “vaporiser” is used in a very vague manner, it is necessary to state that in the classification here adopted the category “engines fitted with vaporisers” indicates only engines in which the fuel enters the cylinder before compression. The numerous designs of engines which possess vaporising chambers in the cylinder head, and inject the fuel towards the end of the compression stroke, are treated in the section on engines fitted with atomisers. Such engines are sold under a variety of names, such as “crude oil engines,” “heavy oil engines,” or “semi-Diesel engines.” The engines fitted with carburetters and vaporisers operate on the constant volume cycle, while the engines fitted with atomisers attempt the constant pressure cycle. However the classification of liquid fuel engines is made, there are always designs that will be found to be on the dividing line between two classes. As the design is intimately connected with the type of fuel which may be safely employed on the engine, it is

necessary to make allowances for any peculiarities of design when valuing a fuel for use on any particular engine.

Liquid fuel is in many respects the ideal fuel on account of its extreme convenience in handling and storing, its comparative purity, and its high heat value. If we compare the properties of our most important solid fuel—coal, with the most important liquid fuel—petroleum, we find that the latter possesses many striking advantages.

The heat yielded by one pound of average coal when burned is about 12,000 B.Th.U., whereas one pound of petroleum yields 18,000 B.Th.U. Petroleum oil occupies less space per unit weight than coal. One ton of petroleum fuel oil occupies about 40 cub. ft., whereas one ton of coal occupies about 43 cub. ft. Oil can be stored in almost any position, and easily transferred by pumping. This latter point is of great importance in marine work, where oil can be stored in double bottoms and other positions which would be quite inaccessible for coal bunkers. This convenience in the storage of oil enables designers to utilise parts of ships for cargo which would otherwise be occupied by coal. Liquid fuel is practically free from ash, whereas the ash contents of coals are frequently as much as 15 per cent. Liquid fuels are more convenient, cleaner, and more rapid to transport, as they may be conveyed by pipe lines.

These advantages apply to oil when used as fuel for external combustion, but when it is employed for internal combustion the advantages are much greater. Coal cannot be directly burned in an internal combustion engine, and when it is burned under steam boilers, and the steam is utilised in a steam engine or turbine, only 10 per cent. to 20

per cent. of the heat is converted into power. When oil is burned in an internal combustion engine of the semi-Diesel or Diesel type, 30 per cent. to 40 per cent. of the heat is transformed into power. Taking average figures, we find that one pound of oil used in an internal combustion engine will yield the same amount of power as three pounds of coal burned under a steam boiler.

The Diesel engine is very heavy in proportion to the power which it develops, but it does not require boilers, economisers, and condensers, which advantage has made this type of engine successful for submarine propulsion. Semi-Diesel engines are also heavy, but with carburetting engines the weight per brake horse power is exceedingly low, and when the weight of the fuel is also taken into consideration, the total is much lower than that of any other source of power. The lightness and efficiency of the petrol engine and its fuel has greatly facilitated the construction of the automobile, and has made the aeroplane and dirigible airship possible, thus being responsible for some of the most remarkable conquests by mankind over the forces of nature.

The enormous success of engines which burn liquid fuels has resulted in a serious shortage of those fuels, which must to some extent interfere with the use of such engines. This difficulty can only be overcome by a revision of the wasteful methods which have hitherto marked the use of all fuels, and such a revision necessitates a thorough understanding of the entire subject. The development of liquid fuel engines may be seriously retarded unless steps are taken to provide additional supplies of fuel. There is, however, no doubt that by suitable measures the amount of liquid fuel available can be enormously

increased. The high price of imported fuels during the war resulted in many improvements tending towards economy, such as the use of heavier grade spirits in petrol engines, heavier fractions in vaporising engines, and the use of coal tars and coal tar distillates in Diesel engines. The number of possible substitutes for the fuel oils at present principally used is great, and many developments must be forthcoming, if the subject but receives the necessary attention, and the necessary experimental work.

LIQUID FUELS

PART I

CHAPTER I

PETROLEUM

PETROLEUM is found in the earth's crust at varying depths. It is occasionally found lying on the surface of water in pools, and may be removed by skimming; but more usually drilling and pumping are necessary in order to obtain the oil in any quantity. It frequently exists in the earth under pressure, and when opened out by drilling, forces its way up the boring to the surface without the need of pumping. In such cases the wells are known as "gushers." In any case the oil is removed by railway tanks, pipe lines, tank steamers, or in barrels to the refinery, where it undergoes further treatment. Very little of the oil reaches the consumer in the crude state. The oil is generally found in strata of conglomerate or of oil sands.

Petroleum oil is generally accompanied by gaseous hydrocarbons, known as natural gas, and solid hydrocarbons (paraffins).

The apparatus employed for drilling is very ingenious, but considerations of space do not allow of a detailed description being given here. The borings are generally 4 to 12 in. in diameter, and vary in depth from a few feet to as much as 4,000 ft.

Petroleum wells may be drilled by percussion, as in the American and Canadian-Galician systems, or by the rotary system. By the American and Canadian methods the strata

are penetrated by blows from a chisel-shaped bit, which is suspended from a cable in such a manner that a hammering effect can be produced upon the bit. In the rotary system a drill is attached to the lower end of a series of tubes, and is rotated by an engine situated on the surface. In both systems means are provided for the removal of sand and fragments of the rock traversed in sinking the bore.

A full account of the apparatus and procedure of petroleum mining may be found in Sir Boverton Redwood's book, "A Treatise on Petroleum."

Origin of Petroleum.—The many theories which have been propounded to account for the origin of petroleum may be classified in three main groups, namely: Theories of Inorganic Origin; the Terrestrial Vegetation theory, and the Marine Animal theory.

The inorganic theories are based upon the action of water on metallic carbides yielding hydrocarbons. Much experimental evidence has been brought forward in support of these theories, but they have not received the support of geologists nor of petroleum experts.

The production of hydrocarbon oils by the action of heat on peat, lignite, and coal has led to the proposition of many theories of the origin of petroleum. The formation of some petroleum may be accounted for in this way.¹ Geologists, however, point out that coal fields and oil fields do not generally occur in such positions as to suggest the probability of oil originating from coal.

The formation of petroleum by the action of heat and pressure on the remains of marine animals appears to be quite possible, and this is the theory most supported by geologists. Engler² considers the action to have taken place in stages by fermentation and hydrolysis, then elimination of water and carbon dioxide, followed by cracking.

Petroleum is widely distributed throughout the earth's crust, and the relative importance of the various fields can best be gathered from the following table of productions³ for the years 1913, 1915, and 1917.

¹ Redwood, "A Treatise on Petroleum," p. 274.

² Engler, *Zeits. f. angew. Chem.*, 1908, p. 1590.

³ U.S. Geological Survey.

Country.	Barrels of 42 U.S.A. Gallons.		
	1913.	1915.	1917.
United States	248,446,230	281,104,104	335,315,601
Russia - -	62,834,356	68,548,062	69,000,000†
Mexico - -	25,902,439	32,910,508	55,292,770
Roumania - -	13,554,768	12,029,913	2,681,870
Dutch East Indies -	11,966,857	12,386,808*	12,928,955*
India - -	7,930,149	7,400,000†	8,500,000†
Galicia - - -	7,818,130	4,158,899	5,965,447
Japan - - -	1,942,009	3,118,464	2,898,654
Peru - - -	2,133,261	2,487,251	2,533,417
Germany - - -	995,764†	995,764	995,764
Egypt - - -	94,635	221,768	1,008,750
Trinidad - - -	503,616	750,000†	1,599,455
Canada - - -	228,080	215,464	205,332
Italy - - -	47,256	39,548	50,334
Other countries -	270,000†	526,120†§	1,674,737†‡
Total - - -	384,667,550	426,892,673	500,651,086

* Includes British Borneo.

† Estimated.

‡ Includes Argentina and Cuba.

§ Includes 516,200 barrels produced in Argentina.

¶ Quantity marketed.

The following figures of the world's oil production for 1918 are given by the Deutsche Petroleum Aktiengesellschaft :—

	1918.
United States - - -	46,179,183 metric tons.
Russia - - -	4,576,500 „
Roumania - - -	1,242,381 „
Galicia - - -	772,946 „
Mexico - - -	10,000,000 „
Dutch East Indies - -	1,800,000 „
India - - -	1,150,000 „
Japan - - -	400,000 „
Other countries - -	1,200,000 „

World's total - - - 67,321,010 metric tons.

Many of the items are obviously estimated.

Chemical Nature of Petroleum.—Petroleum mainly consists of the elements carbon and hydrogen, but also contains small quantities of sulphur, oxygen, and nitrogen; other elements being present only in minute quantities.

The main portion of crude petroleum consists of hydrocarbons (bodies containing carbon and hydrogen only); the

other elements present may be considered as impurities. The oxygen is present in the form of oxygen-containing organic compounds; nitrogen mainly as amines; and sulphur mainly as mercaptans and thio-ethers.

Hydrocarbons may be divided into series possessing general formulæ by means of which the number of hydrogen atoms present in the molecule may be determined, if the number of carbon atoms be stated. Each series possesses its own chemical peculiarities. The various series may be divided into three main types: Aliphatic, Aromatic, and Hydro-aromatic. Petroleum always contains hydrocarbons of each of these types, but the proportion of each type varies according to the origin of the petroleum. Coal tar products (which will be dealt with later) also contain these classes of hydrocarbons.

The more important aliphatic hydrocarbons are members of one of the following two series:—

Paraffins. (General formula: C_nH_{2n+2} .)			Olefines. (General formula: C_nH_{2n} .)		
Methane	-	CH_4	Ethylene	-	C_2H_4
Ethane	-	C_2H_6	Propylene	-	C_3H_6
Propane	-	C_3H_8	Butylene	-	C_4H_8
Butane	-	C_4H_{10}			
Pentane	-	C_5H_{12}			

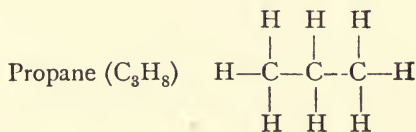
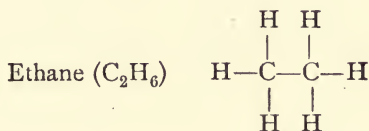
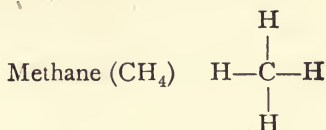
These series may be continued indefinitely.

The physical properties of the members of these series vary by fairly regular steps, as is seen in the following table of properties of the paraffin series of hydrocarbons:—

Name.	Formula.	Boiling Point.	Melting Point.	Specific Gravity.
Methane	CH_4	-160° C.	-186° C.	$\cdot 415$ at -160° C.
Ethane	C_2H_6	-93 ,	-172 ,	$\cdot 446$ at 0° C.
Propane	C_3H_8	-45 ,	...	$\cdot 536 \text{ ,}$
Butane	C_4H_{10}	1 ,	...	$\cdot 600 \text{ ,}$
Pentane	C_5H_{12}	$36\cdot 4^\circ \text{ ,}$...	$\cdot 627 \text{ ,}$
Hexane	C_6H_{14}	$68\cdot 9 \text{ ,}$...	$\cdot 658 \text{ ,}$
Heptane	C_7H_{16}	$98\cdot 4 \text{ ,}$...	$\cdot 683 \text{ ,}$
Octane	C_8H_{18}	$125\cdot 6 \text{ ,}$...	$\cdot 702 \text{ ,}$
Decane	$C_{10}H_{22}$	173 ,	-31° C.	$\cdot 730 \text{ ,}$
Hexadecane	$C_{16}H_{34}$	$287\cdot 5 \text{ ,}$	18 ,	$\cdot 775$ at M.P.
Pentatriacontane	$C_{35}H_{72}$	331 at 15 mm.	75 ,	$\cdot 782 \text{ ,}$

It has been found, by chemical research which cannot be detailed here, that the carbon atoms in the molecules of

these compounds are bound together in the form of chains, as here shown :—



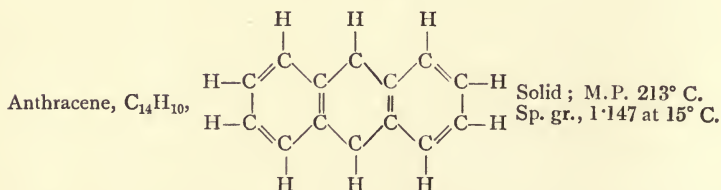
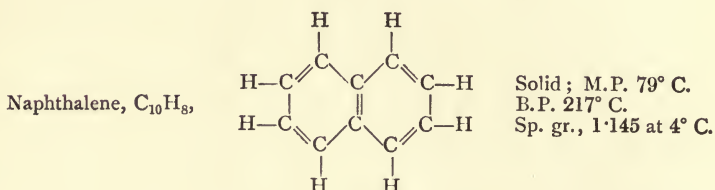
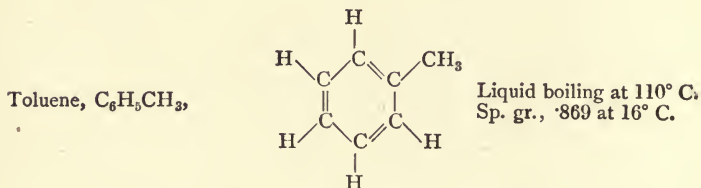
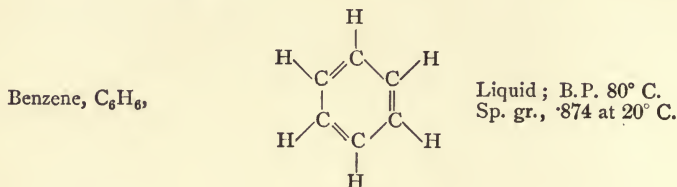
On account of this structure such compounds are frequently called “chain compounds.” The way in which the carbon atoms are attached one to the other is of the highest importance, as this greatly influences the properties of the compound.

The olefines are also chain compounds, but do not contain so great a proportion of hydrogen as the corresponding members of the paraffin series. Paraffins can be prepared from the olefines containing the same number of carbon atoms by the addition of hydrogen (two atoms to each molecule), under suitable conditions.

As hydrogen cannot be introduced into paraffins, it is usual to call these compounds “saturated,” while on account of their property of receiving hydrogen the olefine molecules are known as “unsaturated.” We therefore see that a paraffin is a saturated aliphatic hydrocarbon, while an olefine is an unsaturated aliphatic hydrocarbon.

The aromatic compounds have the carbon atoms disposed in the form of a ring. Their structure will be seen from

the accompanying formulæ of some of the more important members of this group :—

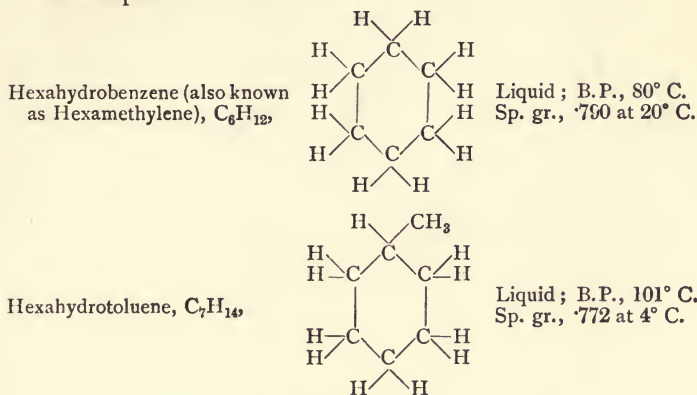


The properties of these compounds are entirely different from those of the members of the aliphatic series. For example, hexane boils at $68\cdot9^{\circ}C$. and possesses a specific gravity of $\cdot 658$ at $20^{\circ}C$., whereas benzene, containing the same number of carbon atoms, boils at $80\cdot4^{\circ}C$., and possesses a specific gravity of $\cdot 874$ at $20^{\circ}C$.

The third class of hydrocarbons are the hydro-aromatic compounds. These, which are also known as naphthenes, again possess different properties, though from the fuel user's point of view they are more closely allied with the aliphatic bodies than with the aromatic compounds. They may be

considered as compounds obtained from benzene by the addition of six atoms of hydrogen.

Example :—



The members of these three types exhibit different properties. For the present it will suffice to note that :

- (1) The aliphatic compounds have the lowest specific gravities : the aromatic bodies are heaviest ; while the naphthenes or hydro-aromatic compounds are intermediate when compounds of approximately the same boiling point are compared.
- (2) The higher members of both the aliphatic and hydro-aromatic classes contain roughly two atoms of hydrogen for each atom of carbon. The aromatic compounds contain a much lower proportion of hydrogen.

Petroleum mainly consists either of aliphatic hydrocarbons, as is the case with Pennsylvanian petroleum, or of hydro-aromatic compounds, as in most Caucasian petroleum. The composition of petroleum, according to Neith, averages—

Carbon	-	-	-	84.5 per cent.
Hydrogen	-	-	-	12.5 „
Oxygen	-	-	-	2.0 „

The sulphur content is generally from $\cdot 4$ per cent. to $1\cdot 0$ per cent., but in the case of Mexican and Texas oils it reaches $3\cdot 0$ per cent., and sometimes exceeds this figure. Nitrogen is only present in small quantities, and is of minor importance.

Petroleum also frequently yields small quantities of ash.

The production of petroleum has been increasing during the last twenty years, but recently the demand has developed more rapidly than the output, as a result of which prices have risen rapidly.

In the future the supplies may be increased by the discovery of new fields, and by the more economical working of old fields, but the output cannot continue to increase as rapidly as it has done in the past. There may be, however, a great increase in the output of lighter products, as processes for the conversion of heavy grade oil into light spirit have improved vastly during recent years.

The world's production of petroleum in 1913 was 384,667,550 barrels, and in 1917 was 500,651,086 barrels.

The development of the production of petroleum is best seen from the statistics of the United States, where the petroleum industry originated, and which, during 1913, produced 64 per cent. of the total output of the world.

1859	-	-	2,000 barrels.
1860	-	-	500,000 "
1870	-	-	5,260,745 "
1880	-	-	26,286,123 "
1890	-	-	45,823,572 "
1900	-	-	63,620,529 "
1910	-	-	209,557,248 "
1913	-	-	248,446,230 "
1914	-	-	265,762,535 "
1915	-	-	281,104,104 "
1917	-	-	335,315,601 "

The figures of the world's petroleum production for a few recent years are :—

1901	-	-	21,709,000 metric tons.
1909	-	-	40,070,832 "
1910	-	-	43,986,531 "
1911	-	-	46,526,334 "
1912	-	-	47,047,000 "
1913	-	-	51,704,951 "
1914	-	-	53,550,267 ¹ "
1915	-	-	57,298,786 "
1917	-	-	66,754,364 ¹ "
1918	-	-	67,321,010 ¹ "

¹ Approximate.

Crude Petroleum.—Petroleum occurs as a black or brown liquid, often accompanied by soft crystals of wax. The properties of the crude product vary greatly, and are mainly dependent on the locality. It may be mentioned, without entering into detail, that Pennsylvanian and Ohio oils are generally low in gravity, rich in light products, and low in viscosity, that is to say "thin." The Mexican, South American, and Texas oils are generally of high specific gravity and viscous, whilst Russian, Galician, and Roumanian products occupy an intermediate position. Oils from Burma, Sumatra, and Assam approach more nearly to the Pennsylvanian products in composition. There are, however, many exceptions to the above generalisations.

Distillation of Petroleum.—Petroleum as it comes from the earth is seldom used in the crude state. Its treatment may be divided conveniently into two sections—distillation and refining. The former separates the various products according to their boiling points, while the latter removes sulphur, oxygen, and nitrogen-containing bodies, together with other undesirable constituents.

The mode of procedure, and the apparatus used for the distillation, vary on the different oil fields: the general principle is, however, the same, and it will suffice to examine American practice only.

The most common still is the horizontal cylindrical type, heated by fire on the under side. These stills are constructed to take charges of as much as 4,000 gals. The upper portion of the still is generally exposed to the air, and provided in the centre with a dome, through which the vapours pass before leaving the still. The condenser is connected with the dome by a pipe of wide diameter, the vapours being condensed in a coil immersed in a water tank.

On charging and heating the stills, the more volatile products distil over first, and may be collected in such fractions as the distiller requires.

The products of the first distillation are naphtha or spirit, the boiling temperature being up to 150°C ., and illuminating and burning oil (kerosene), 150°C . to 300°C . At this point it is usual to stop the distillation and run off the residue, which may be worked up by filtration and distillation for

paraffin wax, lubricating oils, gas oils, etc., or the residue may be sold as fuel oil without further treatment. The temperature at which the distillation is stopped naturally affects the quantity and quality of the residue. The first two fractions may be redistilled to remove impurities passed over during the first distillation. The naphtha fraction is then redistilled in special stills, heated by steam coils, and provided with fractionating columns. These columns contain baffling and scrubbing devices which cause a more efficient separation of the bodies of various boiling points. The products of this distillation may be distilled again, or passed on to the refining plant, as is done with the fraction 150°C. to 300°C. , obtained from the previous distillation.

The most volatile fraction obtained from these distillations is condensed under pressure, and stored in cylinders, on account of its extreme volatility. Other volatile products are obtained. The first important fuel is benzine, which distils between 70°C. and 120°C. This possesses a specific gravity of .72, and finds use as motor spirit. The other portions obtained from the original distillate up to 150°C. are used for industrial and fuel purposes, or mixed with heavy grades of motor spirit. These distillates, and the kerosene (150°C. to 300°C. ; sp. gr. about .800), are each subjected to further purification by mixing with sulphuric acid, and agitation of the mixture. The liquid is allowed to settle, and the sulphuric acid, which falls to the bottom of the agitator, is drawn off. Sulphuric acid removes many of the sulphur compounds, all basic bodies, and several unstable hydrocarbons.

The oil is next washed with caustic soda, which removes any acid left from the previous wash, together with acidic bodies present in the oil. A final wash with water removes any caustic soda left in the oil.

Cracking.—It has been found by petroleum refiners that if the oil be subjected to violent heating in the absence of air, or be cooled and condensed from the upper portion of the still so as to fall into the hot residue, a larger yield of volatile products can be obtained than by direct distillation. This means of increasing the production of the lighter hydrocarbons is technically known as "cracking," and is possible

on account of the instability of some of the more complex hydrocarbon molecules. These compounds split under the influence of high temperatures and form simpler hydrocarbons, which possess lower boiling points. Gaseous hydrocarbons are generally present among the products of cracking, and free carbon is often deposited during the process. Cracked oils generally contain a larger proportion of unsaturated hydrocarbons (olefines) than straight distilled oils, and therefore possess a higher gravity in relation to their

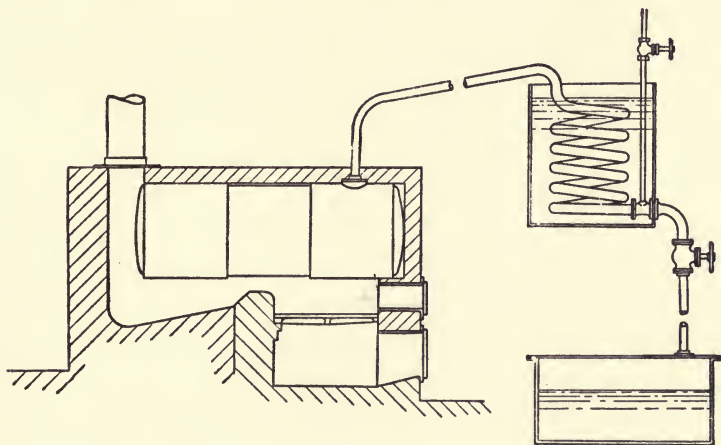


DIAGRAM OF THE BURTON APPARATUS FOR CRACKING HEAVY OILS.

FIG. 1.

distilling temperature. They possess a disagreeable odour, require more sulphuric acid during their refining, and have a comparatively high bromine value. The yield of motor spirit from an average crude oil may easily be doubled by the adoption of cracking processes.

The process of "cracking" has undergone considerable development during recent years, and is at present being conducted on an enormous scale in the United States. A slight cracking is produced by the rapid cooling and heating which takes place when oil falls back from the cool fractionation column and still walls into the hot residue which lies at

the base of the still. By the application of both heat and pressure, the process becomes much more effective. Thorpe and Young made classical researches in 1871 into the action of combined heat and pressure on shale oils, and the cracking of petroleum may be said to be based on the results of their investigations.

In 1889 Redwood and Dewar patented an apparatus for both distilling and condensing the oil under pressure; this to a large extent prevents the escape of the gases which are soluble in the cracked distillate. The Burton process at present worked by the Standard Oil Company is very similar to that given in Redwood and Dewar's patent. The accompanying illustration, Fig. 1, shows a diagram of the Burton apparatus. The apparatus consists of a still for residue in course of treatment, fire-box, safety valve for relieving gas pressure, condenser coil, shut-off valve and receiver for "cracked" product. A very large number of patents have been taken out to protect various processes for the cracking of petroleum. A few of these are working successfully at the present time. A very ingenious device for this object has been invented by Mr W. A. Hall.¹ The petroleum is passed at a pressure of 50 to 75 lbs. per square inch through one-inch tubes, at a speed of over 5,000 ft. per minute, the tubes being situated in a furnace. The temperature inside the tubes attains about 550° C. The oil is discharged from these tubes through a constricted aperture into a pipe of about 12 in. diameter, and impinges on a baffle as it enters the larger tube, whereby its kinetic energy is converted into heat, causing a rise in temperature of about 30° C. The actual cracking takes place in the wide pipe. After undergoing a process of fractional condensation, the more volatile constituents which remain in the gaseous state are passed through a compressor and then condensed. Mr Hall suggests, as a future source of petrol in Great Britain, the production of cracked spirit in specially constructed oil gas plants, to be worked in gas works, and estimates that motor spirit could be produced as a by-product at a cost of 5d. per gallon.

¹ W. A. Hall, *Journ. Inst. Petr. Technologists*, 1915, pp. 1-147.

Processes have been patented recently, in which steam is mixed with the oil during the cracking process, the object being to decompose the steam with the resulting hydrogenation of the oil. The direct introduction of hydrogen by means of catalytic agents (metallic nickel being a favourite one) has not met with any great success.

When it is desired to distil the heavier portions of the oil with the minimum amount of decomposition, as in the preparation of lubricating oils, the removal of the products of distillation may be assisted by passing superheated steam into the still, or by distilling *in vacuo*.

Uses of Petroleum Products.—The more volatile products of petroleum distilling below 60° C. find use for various industrial purposes. Products distilling 60° C. to 150° C. are available for use in engines fitted with carburetters (petrol engines) and are found in the various grades of petrol. The lightest products with lowest boiling points are used in special petrol for racing, and for increasing the volatility of heavier spirits. The usual commercial products are frequently divided into two or three qualities, the prices of which fall with decreasing volatility. These products also find use to a considerable extent as solvents in rubber works, dry cleaning plants, and many other industrial undertakings.

The kerosene or paraffin oil fraction (150° C. to 300° C.) finds use mainly for illuminating purposes and as fuel for engines fitted with vaporisers.

Heavier distillates of petroleum, such as solar and gas oils (sp. gr. about .850), find an extensive field of application in the manufacture of oil gas, a product of high luminosity used for enriching coal gas. Such products are also used as fuel for heavy oil engines.

The crude oil, depetrolised crude oil, and still residuum all find use in Diesel and other types of heavy oil engines fitted with atomising devices. In some cases they are worked for lubricating oils and for petroleum coke.

Yield of Petroleum Products.—The yield of the various types of products is dependent on the crude oil employed. Some crude oils will yield only minute quantities of petrol and small amounts of kerosene, whereas with a high grade Penn-

sylvanian crude it is possible by using the cracking distillation process to obtain 80 per cent. of burning and illuminating oils.

In order to find the yield of the various products from a crude oil it is necessary either to consult tables for that particular oil, or to make a special analytical examination.

The quantities of the various petroleum products used in this country can be seen from the statistics of petroleum imported into the United Kingdom (p. 191).

CHAPTER II

SHALE OIL AND ITS PRODUCTS

THE oil shale industry was founded in France about the year 1840, and in 1850 the distillation of bituminous coals with a view to obtaining paraffin wax and oils was the subject of a patent by Dr James Young, of Glasgow. After working for some time on a highly bituminous mineral known as Boghead coal, or Torbanehill mineral, Young turned his attention to bituminous shales. This resulted in the founding of the Scottish shale industry. Shale is found in Scotland, England,¹ France, New Zealand, New Brunswick, Nova Scotia, Serbia, and Spain. The Scottish is the most important shale industry at the present time. The production of crude shale oil in Great Britain during 1917 was 57,285,024 gals., or rather under 230,000 tons.

Oil shale is a dark grey or black mineral, with a laminated fracture and a specific gravity of about 1.75. According to Redwood,² the proportion of mineral matter is usually about 73 per cent., but it is occasionally as high as 80 per cent. On account of its high ash content it does not coke when heated to redness in a closed vessel. The average yield of crude oil is about 23 gals. per ton of shale, though shales occasionally yield as much as 60 gals. of oil per ton.

Shale may be considered as a product formed by the diffusion of petroleum or a similar substance into a porous clay.

Shale is mined by much the same means as are employed in coal mining. It is then broken up by machinery and placed in retorts, where it undergoes destructive distillation.

The retorts are of various types; horizontal, inclined, and vertical designs, working both on the intermittent and continuous systems, have been employed. The retorts work at a dull red heat (about 485° C.), and it is common to employ

¹ A company has recently been formed to exploit shale deposits found in Norfolk.

² Redwood, "Treatise on Petroleum."

the retorted shale as fuel, on account of it containing a considerable quantity of carbon.

About 3,000 cub. ft. of gaseous products are generated from each ton of shale. These are passed through a series of vertical pipes, the lower ends of which are provided with outlets for the condensed products. Ammoniacal liquor and crude oil are condensed together, and are separated by allowing them to settle, when the oil rises to the top, and each product can be removed by pumping. The gas produced is stripped of condensable products by scrubbing or by cooling under pressure. After separation from the ammoniacal liquor the oil is known as crude shale oil.

The crude oil is refined by repeated distillation, the treatment resembling that of petroleum refining. Washing with sulphuric acid and caustic soda is employed as a further means of removing some constituents.

The first distillation yields green naphtha, green oil, and still coke. After further treatment, the naphtha mainly goes to form motor spirit.

From the green oil are obtained solid paraffin, burning oils for lamps, fuel oils, gas oil (for carburetted water-gas plants), and lubricants. The still coke finds use as a smokeless fuel.

The fuels available for internal combustion engines are the naphthas, which find use as motor spirit; the lamp oils and special fractions similar to lamp oils, which are available for engines fitted with vaporisers; and the gas oils, which may be used in Diesel and semi-Diesel oil engines. Crude shale oils vary in composition, but apart from economic reasons, they do not form good fuels, as the proportion of light products is sufficiently large to make them dangerous to handle, as is shown by their low flash points, and also makes them somewhat too rapid in combustion when employed in such heavy oil engines as are capable of burning them. The oils are rich in unsaturated hydrocarbons (olefines), but this does not interfere with their use in internal combustion engines. As fuels they very closely resemble petroleum products.

CHAPTER III

COAL TARS AND THEIR PRODUCTS

Raw Tars.—When coal is heated to redness in an enclosed vessel it yields volatile products and a residue of coke. When the volatile products are cooled, tar and water condense and are deposited and gas passes on.

The nature and quantity of tars produced by the carbonisation of coal are influenced by four main factors:—

1. The type of coal employed.
2. The maximum temperature attained in the carbonising chamber.
3. The speed at which this temperature is attained.
4. The speed of removal of volatile products.

1. Coal varies considerably in composition, and certain kinds (*e.g.*, anthracite) are entirely unsuitable for carbonisation. The “gas coals” yield moderate quantities of tar. Cannel coals and highly fatty coals yield comparatively large quantities of low gravity tar.

2. High maximum temperatures tend to form high gravity viscous tars, rich in aromatic hydrocarbons and “free carbon.”

3. Rapid heating decomposes the aliphatic compounds, thereby yielding small quantities of high gravity viscous tars, mainly consisting of aromatic compounds.

4. If the speed of removal of volatile products be slow, this causes further decomposition to take place on the heated retort walls. This decreases the proportion of aliphatic products, and gives heavy viscous tars, rich in free carbon and aromatic bodies.

Low maximum temperatures, slow heating of the retort or chamber, and rapid removal of volatile products, all tend towards the production of large yields of thin tar, containing little free carbon, and consisting largely of aliphatic bodies.

The tars produced under such conditions resemble petroleum much more closely than tars produced at high temperatures with rapid heating and slow removal of the volatile products.

The methods by which coal is carbonised may be divided into three groups :—

1. Processes for gas manufacture.
2. Processes for coke manufacture.
3. Miscellaneous processes.

Both raw tars and the products obtained by their distillation have been used as fuel for internal combustion engines. Prior to the war they were not employed to any large extent in this country, but in view of the steady increase in the price of petroleum products during the last ten years they will certainly retain an important position as a source of fuel in the future. In France, and more particularly in Germany, where high import duties on petroleum products exist, the use of tars and tar oils has become general.

Tars Produced by Gas Manufacture.—It has been shown how the composition of coal tars varies according to the conditions prevailing in the carbonising chamber. These conditions are generally inherent in the type of plant, and it is therefore found that the nature and yield of tar is dependent upon the type of retort. Retorts may be horizontal, inclined, or vertical, the horizontal being the oldest type. Modern installations are most frequently of the vertical type.

According to Kraemer¹ the average values of the more important constituents of German gas works tars are as follows :—

Benzol and its homologues	-	C_nH_{2n-6}	2.50 per cent.
Phenol " "	-	$C_nH_{2n-7}OH$	2.00 "
Pyridine bases	-	$C_nH_{2n-7}N$.25 "
Naphthalene and acenaphthene	-	C_nH_{2n-12}	6.00 "
Heavy oils	-	C_nH_n	20.00 "
Anthracene and phenanthrene	-	C_nH_{2n-18}	2.00 "
Asphalt (soluble portion of pitch)	-	$C_{2n}H_n$	38.00 "
Carbon (insoluble portion of pitch)	-	$C_{3n}H_n$	24.00 "
Water	-	...	4.00 "
Gases and loss	-	...	1.25 "

¹ *Journ. f. Gasbeleuchtung*, 1891, p. 225.

Horizontal Retort Tar.—Horizontal retort tar is a viscous black liquid containing from 20 to 30 per cent. of free carbon. It is rich in aromatic bodies, being at present the main source of benzene, toluene, naphthalene, and anthracene. The ultimate composition of the dry tar averages about 91 per cent. carbon and 5 per cent. hydrogen, the remaining 4 per cent. being oxygen, nitrogen, sulphur, and inorganic matter. This is the tar richest in carbon, and it possesses a specific gravity in the neighbourhood of 1.20. On account of the high ash and free carbon content it is unsuitable for engine use in the raw state. These properties are due to the high temperatures employed in horizontal retorts, and the very rapid heating to which the charge is subjected.

Inclined Retort Tar.—As might be anticipated, the properties of this product are intermediate between those of horizontal and vertical retort tars.

Vertical Retort Tars.—A large amount of research work has been conducted on the Continent with a view to employing these tars directly as fuels in Diesel engines. These researches have met with considerable success, and at present large quantities of raw tar from Dessau vertical retorts are consumed in Diesel engines in Germany. Both continuous and intermittent vertical retorts yield low gravity, mobile, dark brown tars, which contain some 7 per cent. hydrogen (denoting the presence of considerable quantities of aliphatic bodies), and are almost free from inorganic matter and free carbon. Unfortunately, the majority of installations in this country in which vertical retorts are working alongside other types of plant are in the habit of mixing the tars; a fact which decreases the quantity of suitable tar available for direct use in internal combustion engines.¹ This difficulty will, however, diminish, as the number of vertical retorts in use is steadily increasing. The specific gravity of the tar is generally from 1.05 to 1.10.

Tars Produced in Coke Manufacture.—Coke oven tars vary enormously, and may resemble in composition either the products of horizontal retorts or of vertical retorts.² The nature of the tar is determined by the design of the oven.³

¹ The burning of raw vertical retort tars is described on p. 92.

² Constam and Schläpfer, *Zeits. Ver. d. Ing.*, 1913, p. 1489.

³ The author ran a Mirlees-Diesel engine successfully for six months on Simon Carvé coke oven tar.

Tars from chamber ovens are very similar to vertical retort tars, and have been found to be suitable for Diesel engines.

Tars Produced by Low Temperature Carbonisation.—

Recently several patent processes have been advocated for the low temperature carbonisation of coal. One of the main claims of these processes is the nature of the tar obtained. Several samples of such tars have been examined by the author, and have been found to possess physical properties and chemical compositions which place them, from a fuel standpoint, half-way between a good grade petroleum crude oil and a heavy gas works tar. The hydrogen content of such tars sometimes reaches 10 per cent., while in their other properties they appear to be excellent fuels. The great drawback with these tars is the extreme difficulty which is experienced in removing the water which is in emulsion with the oil. The high tar yields sometimes claimed by advocates of these processes may, to some extent, be explained by the wet tar (containing as much as 50 per cent. water) having been considered as water-free tar. There is at present no considerable quantity of these products on the market. The lighter distilling portions of these tars are suitable for motor spirit.

Blast Furnace and Producer Tars.—When coal is employed as a fuel and reducing agent in blast furnaces a tar is obtained as by-product. This tar contains large quantities of ash, which make it entirely useless as a fuel for internal combustion engines. However, on distillation, it yields a small amount of light products and a large quantity of low gravity oil, which is rich in aliphatic bodies and can be used in Diesel engines. The production of blast furnace tar is small, being only 145,000 tons in the year 1911 in Great Britain.¹ Some tars are obtained from gas producers, but their composition varies largely. The high ash and water contents generally prevent their use as engine fuels.

Oil Gas Tar.—The residue known as carburetted water gas tar or oil gas tar is not a product of coal, but may be most conveniently dealt with here. It is common practice to use oil gas to enrich coal gas for illuminating purposes. Oil gas is produced by violent cracking of gas oil (a high

¹ See Gray and Mellanby, paper presented to Inst. of Engineers and Shipbuilders in Scotland.

boiling distillate of petroleum or shale oil). By this process a residue is obtained, which consists of unchanged oil mixed with a large proportion of aromatic hydrocarbons produced by the cracking of the oil. Some products from the water gas plant which runs in conjunction with the oil gas generator also become mixed with this residue. The result is a light, mobile, reddish-brown liquid possessing a specific gravity of about 1.05, which is an excellent fuel if it be dehydrated, provided that the ash content is not excessive. It is said to consist largely of aromatic compounds.¹

In many cases the tar appears as an emulsion of water and oil, and sometimes it is practically impossible to obtain the tar free from water by settling. The amount of water present in these tars depends on the conditions of working which are maintained in the plant, and if these conditions were scientifically investigated there is little doubt that the tar could be obtained practically free from water by simple settling.²

The clear tar obtained from a suitable plant is an excellent fuel, and would command a far better price on the fuel market than is usually given by the tar distiller.

The production of tars in the United Kingdom for the year 1911 has been estimated to be as follows:—

Coal gas tar	-	-	-	-	785,000 tons
Coke oven tar	-	-	-	-	300,000 „
Producer tar	-	-	-	-	25,000 ³ „

Distillation of Coal Tar.—Of the tars previously described only the gas works and coke oven tars are at present prepared in sufficient quantity to warrant an examination of their distillation products from a fuel standpoint.

¹ Downs and Dean, *Journ. of Ind. and Eng. Chem.*, 1914, pp. 366-370. Also Rittman and Egloff, *Journ. of Ind. and Eng. Chem.*, 1915, p. 705.

² It is claimed to be possible to separate the water by centrifugal treatment of the warmed mixture (*Journal of Gas Lighting*, 1915, pp. 130, 196). Müller has used centrifugal separation as a means of removing water and free carbon from tar (*Zeits. f. angew. Chem.*, 1911, p. 1121).

³ Gray and Mellanby, paper presented to Inst. of Engineers and Shipbuilders in Scotland.

The tars are usually sold by the gas works, and conveyed by tank wagon, pipe line, or barges to a tar distillery.

Though many complex and more economical stills have been designed, it is usual in this country to distil tar in

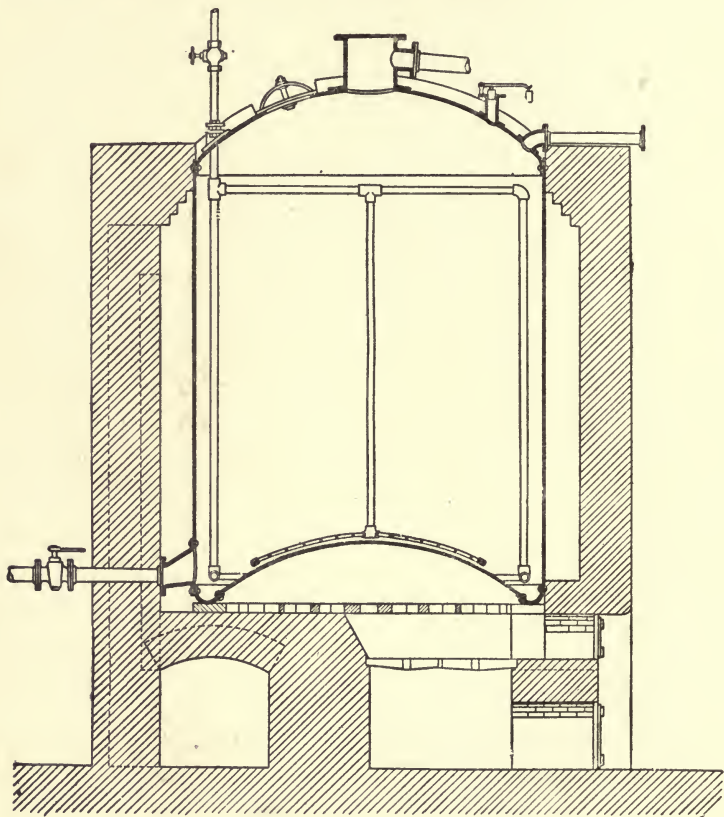


FIG. 2.—Sectional Elevation of English Tar Still.

cylindrical upright stills (see Figs. 2, 3 and 4), which are provided with concave bases. The bases are almost hemispherical in order to allow for expansion of the plates, and to allow the heat more easily to reach the body of the charge.

The stills are usually of 10 to 30 tons capacity, and are made of $\frac{3}{8}$ -in. or $\frac{1}{2}$ -in. wrought-iron plates riveted together.

A dome, or "crown," is situated on the upper portion

of the still, and from this a pipe leads the vapours to a water-cooled worm condenser made of either cast or wrought iron.

The still is heated by a fire under the base; the flues being so arranged as to cause the hot gases to encircle the walls of the still.

It is usual to cover the curved upper portion of the still with brickwork in order to minimise the escape of heat.

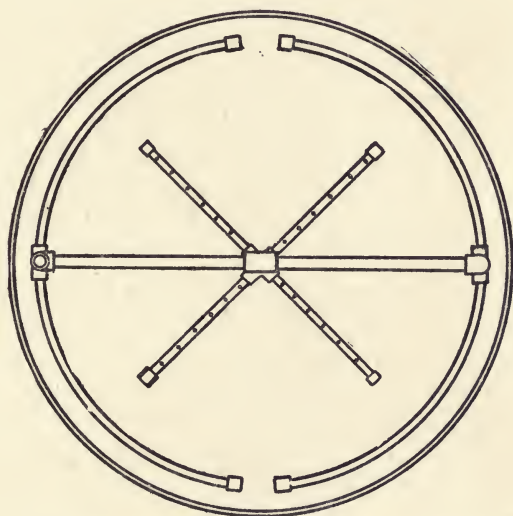


FIG. 3.—Sectional Plan of English Tar Still.

The still is charged and heated gently until the water (which is accompanied by the lighter products) has passed off, as rapid heating during the earlier period of the distillation causes frothing over. When all the water has been driven off the distillation proceeds quickly until the latter stages, when superheated steam is admitted to the still through perforated steam pipes (shown in Figs. 2 and 3) to assist in driving over the heavier oils (mainly anthracene oil).

It is standard English practice to separate the following fractions :—

	Temperature of Distillation.	Sp. Gr. (approximate).	Percentage Yield (approximate).
First runnings or crude naphtha - - -	Up to 110° C.	·920	3·1 percent.
Light oil - - -	110° to 200° C.	·995	1·7 "
Crude carbolic oil -	200° to 240° C.	1·015	3·5 "
Creosote oil - -	240° to 270° C.	1·050	12·0 "
Anthracene or heavy oil	above 270° C.	1·095	9·7 "

A residue of pitch is left in the still.

The first runnings or crude naphtha is accompanied by water, containing ammonia, which settles out, and can be separated by decantation. Benzene and toluene are extracted from the first runnings and from the light oil by repeated distillation, followed by caustic soda and sulphuric acid washes.

Benzene is marketed in various grades of purity, the pure hydrocarbon being generally sold as benzene, while commercial mixtures containing other hydrocarbons are known as benzol. A common product used for petrol engines is the commercial grade known as "90 per cent. benzol." This is not a mixture containing 90 per cent. of benzene, but is a product which, on distilling from a retort, yields 90 per cent. of distillate at 100° C. (benzene boils at 81° C.; toluene at 111° C.). 90 per cent. benzol, or 90's benzol, contains about 75 per cent. of benzene and 25 per cent. of toluene, traces of other hydrocarbons being also present.

The presence of toluene is not objectionable, and is even desirable, as, though it slightly decreases the volatility of the mixture, it lowers the freezing point. Pure benzene solidifies at 6° C., a property which is very undesirable in a motor spirit.

A mixture containing 20 per cent. toluene does not freeze at ordinary cold weather temperatures. The product used by motorists prior to the war was generally either 90 per cent. benzol or some mixture of approximately the same composition.

Though the use of benzol as motor spirit was forbidden during the war, it has come into use in considerable quantities

since the removal of restrictions, and will probably come into further favour when the organisation for marketing benzol is as good as that for marketing petrol.

Benzol and toluol are also prepared in large quantities from coke oven gas. During the war the demand for these products, especially for toluol required for the production of explosives,

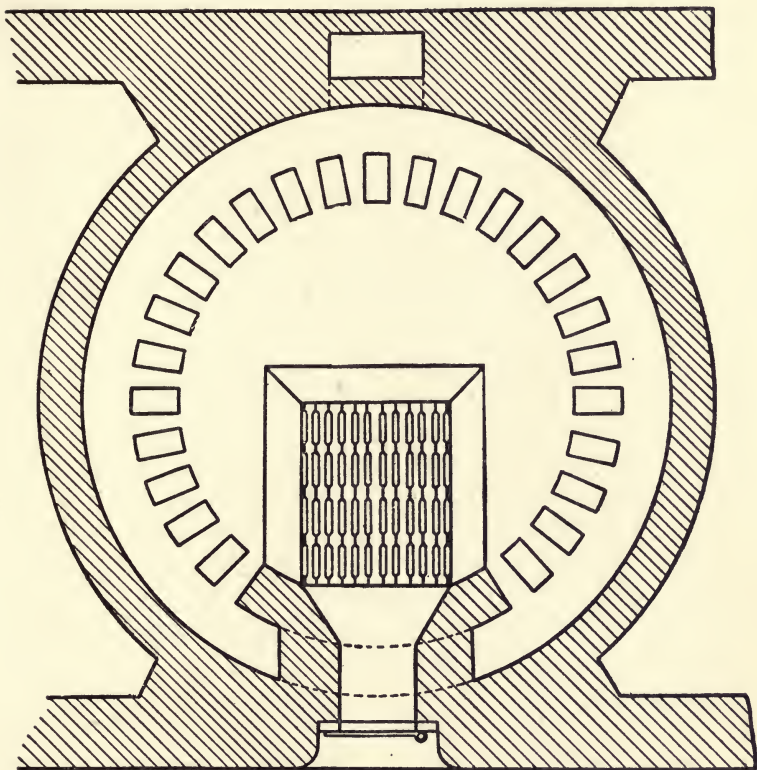


FIG. 4.—Sectional Plan of English Tar Still showing Fire Grate.

became very great, and their extraction from illuminating gas was undertaken by the gas works.

Benzol is recovered from coke oven gas by absorption in either coal tar creosote, blast furnace tar creosote, or a petroleum distillate by means of a scrubbing plant. The benzol is recovered from the benzolised creosote by distillation in continuous column stills. Coke oven gas contains from

0·8 per cent. to 1·6 per cent. by volume of benzol, and yields from 4 to 6 gals. per ton of coal carbonised.¹

The xylenes, of which the three isomeric forms—ortho, meta, and para xylene—are all found in tar, are occasionally separated from the crude naphtha and light oil fractions, though they are generally sold for solvent purposes without complete separation from some of the other hydrocarbons.

Light oil contains by far the larger portion of the xylene, and also yields pyridine when washed with dilute sulphuric acid. Carbolic acid is extracted from light oil by washing with dilute caustic soda.

The carbolic oil consists largely of naphthalene and carbolic acid (phenol), together with cresols and pyridine bases. After the removal of naphthalene a liquid hydrocarbon is left which is sold for disinfectant manufacture, or the carbolic acid is removed, and the residue is added to the creosote oil fraction. Creosote oil contains considerable quantities of naphthalene and cresols, either of which may be extracted as the markets demand. Naphthalene solidifies in the creosote and carbolic oil fractions, and falls to the bottom of the storage tanks in the form of crystals. This action of naphthalene makes it necessary to heat many tar oils in order to prevent obstruction of the pipe lines. The naphthalene is a hydrocarbon, and therefore wholly combustible. Its presence in fuel oils is liable to cause the formation of deposits in the atomisers of Diesel engines.

Naphthalene may be extracted from the crude carbolic oil and the creosote oil by allowing these fractions to cool in storage tanks, when the naphthalene will crystallise out of the solution. After running or pumping off the oil, the resulting deposits of naphthalene are known as “drained salts,” and after treatment in a centrifugal machine a purer product known as “whizzed salts” is obtained. Naphthalene of these grades can be burned in Diesel engines if special arrangements are made for melting the fuel, and if the atomisers are of suitable design. If further purified, naphthalene is suitable for adding to fuel mixtures for use in petrol engines (see p. 60).

¹ G. Taylor, *Journal of Gas Lighting*, 1915, pp. 132, 639.

The yield of naphthalene from coal is about 0·3 per cent. and the refined product possesses the following properties :—

Specific gravity (solid)	-	1·15 at 15° C.
" " (liquid)	-	0·977 at 80° C.
Melting point -	-	80° C.
Latent heat of fusion -	-	36 calories.
Flash point -	-	176° F.
Gross calorific value,	9,668 calories = 17,402 B.Th.U.	
Net " " 9,260	" = 16,668 "	

The spontaneous ignition temperature of naphthalene in oxygen determined in the author's apparatus is 402° C.

Anthracene oil is the highest boiling distillate of coal tar, and is rich in the hydrocarbon anthracene, which, as a fuel, is very similar to naphthalene, and is subject to the same objections.

It is frequently the practice to mix the creosote and anthracene oil fractions. When such oils are sold as fuel, they are generally known to engineers as "tar oil," and are utilised in Diesel engines.

The pitch or residue from the tar is of little interest to internal combustion engineers, but it has been used in solution in creosote for external combustion.

In some cases the lighter products are distilled from the tar, and then the distillation is stopped, and a residue which is liquid at normal temperatures is run from the still.

The residue is known as "treated tar," and is used for road making. The process of removing the water and light fractions is known as "topping," "dehydrating," or "treating," and it is quite within the bounds of possibility that in the future the residue obtained by such a treatment of specially prepared low gravity tars may become a standard fuel for Diesel engines.

It is quite possible that at some future time it may be found to be more expedient and profitable to collect tars at the gas works or coke ovens by a process of fractional condensation, thus obtaining direct from the carbonising plant

a series of products which might closely resemble the products of tar distillation. If this were done, it is certain that by suitable working a large yield of a product suitable for Diesel and semi-Diesel engines could be directly prepared.

The lighter fractions so collected would probably not be sufficiently pure to find use as motor spirits without further treatment, but the treatment required would be less expensive than that at present employed in order to obtain benzol from raw tar.

Reviewing the coal tar distillates, it may be noted that the lightest products, benzol and toluol, have found use as motor spirits, the heavier products, creosote and anthracene oils, as Diesel engine fuels. The intermediate products have not found use as substitutes for the petroleum product known as paraffin oil, and this fact may to some extent be explained by the increase in price of petrol and heavy fuel oil having been greater in recent years than the increase in price of the intermediate petroleum products. Thus there has not been the same incentive or necessity to find a coal tar substitute for kerosene, as has been the case with both the lighter and heavier products.

CHAPTER IV

LIGNITE TARS AND THEIR PRODUCTS

LIGNITE or brown coal is a product formed by the action of heat and pressure upon vegetable matter. The conditions under which lignite has been formed have not been so drastic as those which formed coal, and the properties and composition of lignite are therefore intermediate between those of peat and coal. Lignites are lower in specific gravity than coal, but heavier than peat, and contain from 55 to 75 per cent. of carbon, from 5 to 7 per cent. of hydrogen, and from 10 to 30 per cent. of oxygen. As obtained from the ground, they contain sometimes as much as 50 per cent. of water, and the ash content may reach as high as 15 per cent. Lignites are widely distributed throughout the British Empire, important fields occurring in India, Australia, Canada, and New Zealand. Several beds of lignite are found in Europe. In Saxony the lignite industry is highly developed.

Lignite is often burned under boilers, when it is found to be much inferior to coal. It is sometimes subjected to destructive distillation, tar being the most important product.

The yield of tar varies from 1 per cent. to as high as 12 per cent., but is usually about 5 per cent. The tar has a specific gravity of $\cdot 88$ to $1\cdot 08$, and is semi-solid at normal temperatures, owing to the presence of paraffin wax. It is rich in unsaturated compounds and absorbs oxygen from the air. On distillation lignite tar yields light products suitable for motor spirits, also burning oils, lubricating oils, and paraffin wax.

The products of this first distillation may be further distilled and refined by treatment with caustic soda and acid washes, much in the same manner as coal tar products. The liquid products are a mixture of aromatic and aliphatic hydrocarbons. Benzene and naphthalene are present in considerable quantities, though the specific gravities of the fractions indicate a large proportion of aliphatic bodies. The lightest fractions possess specific gravities of about $0\cdot 75$.

The lighter products make good fuels for engines fitted with carburetters, while the intermediate and heavy products find use on vaporising and atomising engines respectively. The lignite tar distillates, as fuels, are very similar to the corresponding distillates obtained from shale and from petroleum.

The crude lignite tar has been used with complete success as a fuel for Diesel engines, no modification in the design of engine or extra fittings being required.¹

¹ Constam and Schläpfer, *Zeits. Ver. d. Ing.*, 1913, p. 1489.

CHAPTER V

PRODUCTS OF THE CARBONISATION OF WOOD AND PEAT

Wood.—When wood undergoes destructive distillation in a by-product recovery plant charcoal is produced in the oven, and liquid products condense from the volatile portion. A large amount of permanent gas is also produced. According to Pritchard,¹ one cord (4,000 lbs.) of wood yields:—

Best turpentine	-	-	-	40 gals.
Light oils	-	-	-	16 „
Heavy oils	-	-	-	128 „
Charcoal	-	-	-	950 lbs.

The products are dependent upon the type of wood burned.

Methyl alcohol and acetic acid are formed by the carbonisation of hard woods.

The comparative scarcity and high cost of wood prevents the liquid products attaining much importance as fuels, though several are quite suitable. Methyl alcohol can be used in carburetters, while turpentine and the heavier oils are suitable for vaporising and atomising engines.

Peat.—Peat is formed by the decay of vegetable matter under the influence of moisture. It is very widely distributed throughout the world, and enormous quantities are available. Large beds of peat occur in the British Isles. Little has been done towards the utilisation of these deposits on account of the difficulty of drying peat, and the low density and calorific power of the finished product. A great amount of experimental work, both in the laboratory and on a commercial scale, is being done at present with a view to the exploitation of these deposits.

The combustible portion of peat contains 55 to 60 per

¹ *Journal Soc. Chem. Ind.*, 1912, p. 418.

cent. of carbon, and about 6 per cent. of hydrogen and 2 per cent. of nitrogen, the remainder being mainly oxygen.

Peat may be carbonised to a peat charcoal, or it may be treated by a process yielding a semi-carbonised residue which is suitable for the manufacture of fuel briquettes. Certain of the other products of carbonisation serve as a binding material in the briquetting process.

From the results of tests by the Power Gas Corporation¹ the gasification (in producer) of one metric ton of peat has been found to yield:—

Cubic feet of gas at 0° C. and 760 mm.	-	99,000.
(Calorific value per cubic foot	- -	157 B.Th.U.)
Tar	- - - -	110 lbs.
Calcium acetate	- - - -	9 „
Ammonium sulphate	- - - -	165 „

In the case of a Yorkshire peat, F. M. Perkin states that 38 gals. (about 16 per cent.) of tar are obtainable per ton of dried peat. This tar on fractionation yielded:—

1.35 per cent. oil, sp. gr. 0.867.	B.P. below 150° C.
29.90 „ „ „ 0.953.	„ „ 250° C.
50.00 „ „ „ 0.941.	„ above 250° C.

The oils obtained are mostly of the paraffin type.²

E. and F. Bornstein³ found a sample of peat tar to yield 18 per cent. of phenols, 1 per cent. of bases, 34 per cent. of oils, and 47 per cent. of pitch, while Morgan and Scharff⁴ found a sample of crude tar to contain 29.3 per cent. moisture, 52.6 per cent. volatile oils and waxes, 5.8 per cent. pitch, and 11.7 per cent. solid matter. The latter authorities state that peat tars are highly unsaturated, and readily absorb atmospheric oxygen.

The use of peat oils as fuels for internal combustion engines is at present impossible, as no such products are as yet on the market. There appears, however, to be no doubt that the distillates of peat tar would prove suitable for engine use. The use of the raw tar would probably present many difficulties.

¹ Brame, "Fuel—Solid, Liquid, and Gaseous," p. 28.

² F. M. Perkin, paper read before Inst. Petr. Technologists.

³ E. and F. Bornstein, *Journal of Gas Lighting*, 1915, pp. 129, 731.

⁴ G. T. Morgan and G. E. Scharff, *Economic Proc. Roy. Dublin Soc.*, 1915, pp. 2, 161.

CHAPTER VI

ANIMAL AND VEGETABLE OILS

AS animal and vegetable oils are never produced in very large quantities, they can only find use as fuels in special cases, where other fuels are practically unobtainable. They are more liable to chemical change than the hydrocarbon oils, and on account of their oxygen content are lower in calorific power.

They mainly consist of the glycerides of unsaturated organic acids, and have been used on heavy oil engines, but only to a limited extent. Dr. Diesel advocated the use of arachis or earth nut oil as a fuel for the Diesel engine, and the oil that he used showed the following analysis:—

Specific gravity -	-	0.915 at 15° C.
Flash point -	-	233° C. (451° F.)
Hydrogen -	-	11.41 per cent.
Carbon -	-	74.73 „
Oxygen and nitrogen -	-	13.86 „
Net calorific value -	-	8,823 cal. (15,880 B.Th.U.)

The author recently had occasion to test whale oil on a Mirrlees-Diesel engine, and found no difficulty in obtaining excellent running, no modification of engine settings being required. This oil showed the following characteristics on analysis:—

Specific gravity -	-	0.921 at 20° C.
Flash point -	-	over 320° F. = 160° C.
Sulphur -	-	.13 per cent.
Coke -	-	1.27 „
Water -	-	trace
Ash -	-	„
Net calorific value -	-	8,707 cal. (15,673 B.Th.U.)

Further analyses were made on arachis and palm oils,

with a view to their use on Diesel oil engines, by Constam and Schlöpfer. The results are given below :—

	Arachis Oil.	Palm Oil.
Specific gravity - -	·916	·915
Flash point - - -	310° C.	244° C.
Temp. of spont. ignition	400° C.	400° C.
Sulphur - - - -	·1 per cent.	...
Coke - - - -	0·45 „	0·13 per cent.
Water - - - -	trace.	0·14 „
Ash - - - -	„	0·01 „
Hydrogen - - -	11·8 per cent.	11·8 „
Carbon - - - -	77·3 „	76·2 „
Oxygen and nitrogen -	10·8 „	12·0 „
Net calorific value -	{ 8,866 cal. (15,958 B.Th.U.)	{ 8,790 cal. (15,822 B.Th.U.)

The demand for animal and vegetable oils for various industrial purposes is large, so that there is little chance of them assuming much importance in the fuel market, where low prices are essential.

CHAPTER VII

METHYL AND ETHYL ALCOHOLS

THESE two liquids are the lowest members of a large series of organic compounds which are classed as alcohols. The alcohols are compounds containing the hydroxyl group ($-\text{OH}$).

Methyl Alcohol.—Methyl alcohol possesses the chemical formula CH_3OH , and occurs in the distillate obtained by the carbonisation of wood (p. 31). It is available in a crude state as "wood spirit," containing some 80 per cent. of the pure substance. Pure methyl alcohol is a very mobile colourless liquid, boiling at 67°C ., and possessing a specific gravity of $\cdot 789$ at 0°C . On account of its high oxygen content (50 per cent.) it possesses a very low calorific power, 8,320 B.Th.U. net (4,622 calories).¹

As methyl alcohol is not available in large quantity it is of little importance as a fuel, though, provided that certain conditions are maintained, it can be used in carburetter engines.

Ethyl Alcohol.—The supply of ethyl alcohol is much greater than that of methyl alcohol, and is capable of almost indefinite increase. Unlike the other liquid fuels, it is not obtained from deposits which have accumulated in the earth, and therefore there is no danger of the supply becoming exhausted. Ethyl alcohol is formed, together with small quantities of other alcohols, by the process of alcoholic fermentation. By fractional distillation with dephlegmating column it is possible to concentrate the alcohol to about 95 per cent. (by volume). It does not pay commercially to bring the alcohol to a higher concentration, as the removal of the last portion of the water is very expensive.

Pure ethyl alcohol (formula, $\text{C}_2\text{H}_5\text{OH}$) is a colourless mobile liquid with a sweet smell and a burning taste. The

¹ Brame, "Fuel—Solid, Liquid, and Gaseous."

specific gravity of ethyl alcohol (generally called alcohol) is $\cdot 794$, and the boiling point $78\cdot 5^{\circ}$ C. It contains a large proportion of oxygen, 34.74 per cent., which accounts for the low calorific power of 6,362 cal. net (11,452 B.Th.U.).

The properties of alcohol-water solutions of various concentrations are shown in the following table:—¹

PROPERTIES OF ALCOHOL-WATER SOLUTIONS.

Specific Gravity at 15° C.	Percentage Alco- hol by Weight.	Percentage Alco- hol by Volume.	Net Calorific Power.	
			Calories.	B.Th.U.
$\cdot 794$	100.00	100.00	6,362	11,452
$\cdot 809$	95.08	96.85	6,019	10,834
$\cdot 823$	90.02	93.28	5,666	10,199
$\cdot 836$	85.01	89.48	5,318	9,572
$\cdot 848$	80.21	85.64	4,984	8,971

Although alcohol is not used as a fuel to any large extent in this country, it has found use in France and Germany for some time past in specially designed carburetter engines. It was used during the war in large quantities by the German army for motor transport, for which purpose it was mixed with benzol and naphthalene. The importance of alcohol as a fuel lies in its future possibilities as a substitute for petrol.

The commercial success of the use of alcohol as fuel depends largely on the cost of its production, and on the price of the competing motor spirits, petrol and benzene. With petrol at a price so high as during the last three years alcohol should prove an undoubted success.

Alcohol has hitherto been prepared from starch and sugar-containing vegetable matter by means of the yeast cell, but it has been found possible in recent years to prepare alcohol at much less cost from cellulose. Waste sulphite liquor, a by-product from paper manufacture, has been found to be specially suitable as a starting point for the production of alcohol.

According to Professor R. F. Ruttan,² the Standard

¹ Schmitz, "Die flüssigen Brennstoffe," pp. 95 and 97.

² *Journ. Soc. Chem. Ind.*, 1909, p. 1291.

Alcohol Company, which was successfully producing alcohol from 100 tons of dry sawdust daily, claimed that if they increased their plant to 200 tons daily they could produce 90 per cent. alcohol at a cost of 10·8 cents per gallon. By working on a still larger scale the cost could be reduced to 7 cents per gallon.

This plant is stated to yield 20 gals. of 94 per cent. alcohol per ton of dry sawdust. Kressmann¹ obtains 8·54 per cent. of alcohol from white spruce, and 4·98 per cent. from western larch. In the report of the Motor Union Fuels Committee it is claimed that 90 per cent. alcohol can be produced by the fermentation of peat, at a cost of 3d. per gallon. It appears that a Swiss company in the early days of the war succeeded in preparing alcohol from calcium carbide on a commercial scale. Although the coal, obtained from Germany, cost 600 francs per truck load, a pure industrial spirit was prepared for £22. 4s. per metric ton, and a spirit of second quality for £21. 2s., which costs correspond to 19·56d. and 18·6d. respectively per gallon. This installation was capable of producing 7,500 to 10,000 tons per annum.

After the production of the alcohol, it is necessary to add some denaturant to the spirit to render it unfit for drinking. This denaturant must be a substance which it is difficult to remove from the spirit. Pyridine, wood spirit, and certain petroleum fractions are at present used for this purpose. These denaturants have been found to be injurious to the alcohol as a fuel, and the legislation on this point will need revision.

R. J. Friswell stated before the Motor Union Fuels Committee that benzol could be used as a denaturant, as its separation from alcohol is very difficult.² Many other denaturants have been suggested, and no difficulty should be experienced in finding one which will satisfy both the fuel user and the excise authorities. If the use of alcohol as a fuel is to become general in this country, it will first be necessary to modify the Government restrictions on its manufacture and sale.

¹ *Journ. Inst. Engin. Chem.*, 1915, pp. 7, 920.

² Dr Ormandy informs the author that it is possible to separate the benzol from the alcohol by diluting with water, so as to make the alcohol drinkable, though disagreeable in flavour.

The extraction of alcohol from coke oven gas on a commercial scale forms the subject of a paper recently read before the Cleveland Institution of Engineers at Middlesborough by Mr E. Bury, of the Skinningrove Iron and Steel Works. By Mr Bury's process an average yield of 1·6 gals. of alcohol per ton of coal carbonised is obtained, the alcohol being extracted by contact with sulphuric acid. It is estimated that the total weight of coal reduced to coke in this country in 1918 was 14,635,000 tons, and that the application of this process to the whole of this coal would yield 23,416,640 gals. of alcohol, and that the further utilisation of the alcohol produced in the gas works of the country on similar lines would yield 27,000,000 gals. per annum.

PART II

CHAPTER VIII

FUELS FOR ENGINES FITTED WITH CARBURETTERS

THE petroleum industry in its earlier days was mainly directed to the production of medicinal oils and lubricating oils.

The invention of the safety lamp to burn petroleum oil opened up a suitable market for the sale of products boiling from 150°C. to 300°C. (kerosene). As the more volatile spirits had to be removed from both lamp and lubricating oils in order to make the products comply with the flash point regulations, stocks of these low boiling fractions accumulated, and it was not until the development of the petrol engine that a remunerative market could be found for them.

These products (usually called "petrol" in this country) possess a sufficiently high vapour tension to make them volatilise easily in air at ordinary temperatures, thus forming an explosive gaseous mixture, which can be burned in an internal combustion engine. The nature of the fuel and the simplicity of the process lend themselves to the production of engines working at high speeds, and giving high powers for small weight of engine. Such engines find use chiefly for small land installations, marine work, automobiles, aeroplanes, and airships.

The Carburetter.—The petrol engine receives its fuel in a gaseous state, and may therefore be considered as a gas engine. The carburetter mixes the petrol and air in such a manner that the engine is supplied with an explosive mixture of petrol gas and air. The proportion of fuel in the mixture must be variable at the driver's will. While variation of concentration is requisite, it is also necessary

that the carburetter be so designed that the concentration of the mixture supplied to the engine may not be appreciably changed by increase or decrease of engine speed over a very wide range.

It is outside the scope of this work to enter into details of carburetter design. Of the very large number of carburetting devices which have been patented, only a small proportion have been placed on the market, and of these but few survive. The surface carburetter and the jet carburetters of the present day are, however, of interest when considering the quality of fuel which can be used in petrol engines.

The surface carburetter was one of the most popular types in the early days of the petrol engine, and is worthy of note. The principle of the surface carburetter is that the air is drawn in by the "suction" of the engine, and caused to bubble through the petrol by means of tubes or a rose. The mixture of petrol vapour and air thus prepared is then diluted with additional air in the proportion required; the rich gas and extra air supplies each being controlled by a valve.

This carburetter gave good working, and for some time held the field. It had several drawbacks, of which the main one was the formation of a residue of "stale" petrol in the carburetting chamber. This residue was formed by the more rapid evaporation of the lighter constituents of the petrol, leaving those of higher boiling point behind. The heavy portion accumulated until it seriously affected the mixture, when it was necessary to empty the carburetter. The fuel for a surface carburetter required to be exceedingly volatile, and the products obtained from the United States in the days of surface carburetting generally possessed specific gravities in the neighbourhood of '690.

Many attempts were made to employ mechanically operated pumps with sprayers for atomising and volatilising the fuel. Although some of these gave good results they were not sufficiently reliable, and were very complex in construction, leaking of the pump plunger packing being the cause of much trouble. The type almost universally used at the present time is the jet carburetter worked by suction from the engine, a type which yields good results with suitable fuel, and which is exceedingly simple and reliable.

The air is drawn by the engine through a slightly restricted aperture over a jet in which petrol is maintained at a constant level, by means of a chamber containing a float, which automatically operates a needle valve in the petrol inlet pipe. The partial vacuum caused by the suction of the engine suffices to spray the fuel into the air, as in a scent spray, thus making a mixture which is supplied to the engine through the induction pipe. A valve in the induction pipe is controlled by the driver or attendant, and regulates the supply to the engine. Various modifications and additions are used, such as separate small "pilot jets" for slow running and extra air fittings; the principle, however, remains the same. An example of one of the most successful jet carburetters, the Zenith carburetter, is shown in Fig. 5.

This type of carburetter is suitable for a much wider range of fuels than the older surface carburetter, as noselective evaporation can take place. If the fuel contains some difficultly volatile substance, it will still pass

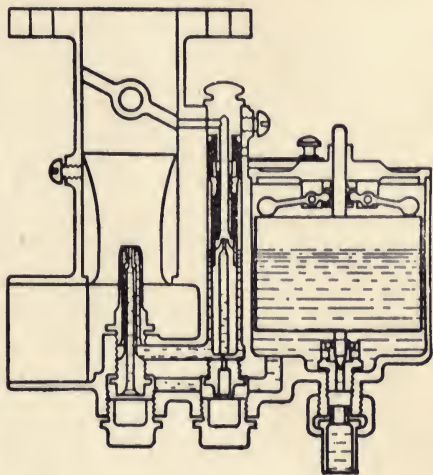


FIG. 5.—Section through Zenith Carburetter.

through the carburetter jet in the form of globules, and there is a great probability that the comparatively high temperature which prevails in the engine cylinder during compression will complete the process of vaporisation before the time of firing.

When the enormous increase in the use of automobiles caused a shortage of petrol, the situation was to some extent relieved by widening the temperature limits when distilling petroleum, so as to make use of some of the products which had been hitherto excluded from the petrol. The specific gravity of motor spirits has, therefore, increased from about

690 to the present 720 for grades of the best quality, while some of the cheaper varieties of spirit exceed 750. The distilling temperatures have, of course, undergone a similar increase.

That the modern carburetter will work on fuels which are difficult to volatilise at ordinary temperatures is shown by the fact that it is possible to run (though not very satisfactorily) on kerosene, provided that the engine first be heated by running on a more volatile fuel.

With certain types of two cycle engines, in which the mixture is compressed in the crank case prior to entering the cylinder, it is the custom to mix lubricating oil with the fuel in order to lubricate the connecting rod and the crankshaft bearings. In such engines the lubricating oil passes through the carburetter.

Although the modern spray carburetter is reliable and efficient, yet it appears to the author that in the near future it must be modified or superseded by some type which shall have a still wider range of fuels. The fitting of hot air intakes, and heaters of the service pipes, to carburetters, and the many other attempts to obtain satisfactory running on kerosene, show the great demand for further improvement in carburetter design.

Properties of Motor Spirit.—The behaviour of any motor spirit can be closely determined by an examination of the following points:—

- Fractional distillation.
- Latent heat of vaporisation.
- Vapour tension.
- Vapour density.
- Explosive range.
- Velocity of flame propagation.
- Temperature of spontaneous ignition, or ignition point.
- Calorific power.
- Specific gravity.
- Air required for combustion.
- Elementary composition.

FRACTIONAL DISTILLATION.—The fractional distillation indicates the boiling points of the constituents of a motor spirit, and therefore gives an approximate idea of the volatility. The correct method of obtaining the volatility is,

however, by means of measurements of vapour pressures. The results of fractional distillation show the temperature range over which the spirit has been collected when it was last distilled by the refiner. Fig. 6 shows curves made by plotting the percentages of distillate from alcohol, petrol, benzol, and paraffin oil against the temperature. This is the most satisfactory method of stating the results of fractional distillation tests.

LATENT HEAT OF VAPORISATION.—The latent heat of vaporisation shows the amount of heat required to vaporise the fuel, and is important in connection with carburetter design. The formation of snow on carburetters is a common effect of the latent heat of vaporisation.

1 gm. of petrol at ordinary temperatures absorbs about 80 cal. of heat on being converted into the gaseous state. For benzol this figure approximates to 100 cal., and for pure alcohol it is over 200 cal.

VAPOUR TENSION.—The vapour tension is a matter of fundamental importance, as it is upon this property that the ease or the possibility of starting a petrol motor depends. The possession of a considerable vapour pressure at normal temperatures is also a necessity in order to obtain good running with flexibility, unless some means of heating the induction air be employed.

Professor V. B. Lewes¹ gives the following figures for the vapour tension of various fractions obtained by redistilling the "benzine" (up to 150° C.) obtained from crude petroleum :—

Specific Gravity.	Vapour Tension in mm.			
	Water at 15° C.			
0.650	-	-	-	2,110
0.680	-	-	-	1,185
0.695	-	-	-	930
0.735	-	-	-	410
0.756	-	-	-	125
0.762	-	-	-	85
0.772	-	-	-	40
0.788	-	-	-	15
0.812	-	-	-	0

¹ V. B. Lewes, Fothergill Lectures, Roy. Soc. of Arts, 1915.

The vapour tensions of petrols vary, the cheaper grades giving lower pressures. Alcohol and benzol give approximately the same vapour tension, but as a larger proportion of alcohol is necessary to yield an explosive mixture with air, greater difficulty in starting is experienced with this substance. The vapour tensions of alcohol, benzol, petrol, and alcohol-benzol mixture (1 : 1) are given in the accompanying curves (Fig. 7).

It is of particular interest that the vapour pressure of mixtures of equal parts of fuels of approximately the same volatility, which are soluble in each other, is often greater than that of either constituent, and frequently approaches the sum of the vapour pressures of the two fuels.

VAPOUR DENSITY.—The density of a vapour of any volatile fuel for use in an engine operating on the standard volume cycle has a bearing on the mean effective pressure, and therefore on the maximum power production. Fuels containing large proportions of components of high molecular weight yield heavy vapours, whilst those containing mostly components of low molecular weight yield lighter vapours. The fuels giving heavy vapours do not occupy so large a portion of the capacity of the cylinder, thereby leaving a greater space for the air necessary for combustion. Thus, assuming the same elementary composition, a fuel of higher molecular weight would give more power, as the engine cylinder would be capable of holding a slightly heavier charge, together with the air necessary for its combustion; *e.g.*, compare an engine running on acetylene with a similar engine running on benzene. In both cases the same weight of air is required per unit weight of fuel, but the density of acetylene gas is one-third that of benzene vapour, therefore the acetylene would occupy three times as much space as a corresponding weight of benzene, leaving a slightly smaller portion of the cylinder available for air. In the case of benzene, therefore, a slightly larger fuel charge may be taken.

EXPLOSIVE RANGE.—If a volatile fuel be mixed with air it is found that, when the proportion of fuel is very small explosion cannot take place. On testing richer mixtures it is found that explosion only takes place over a comparatively small range of proportions, any outside this range not being explosive.

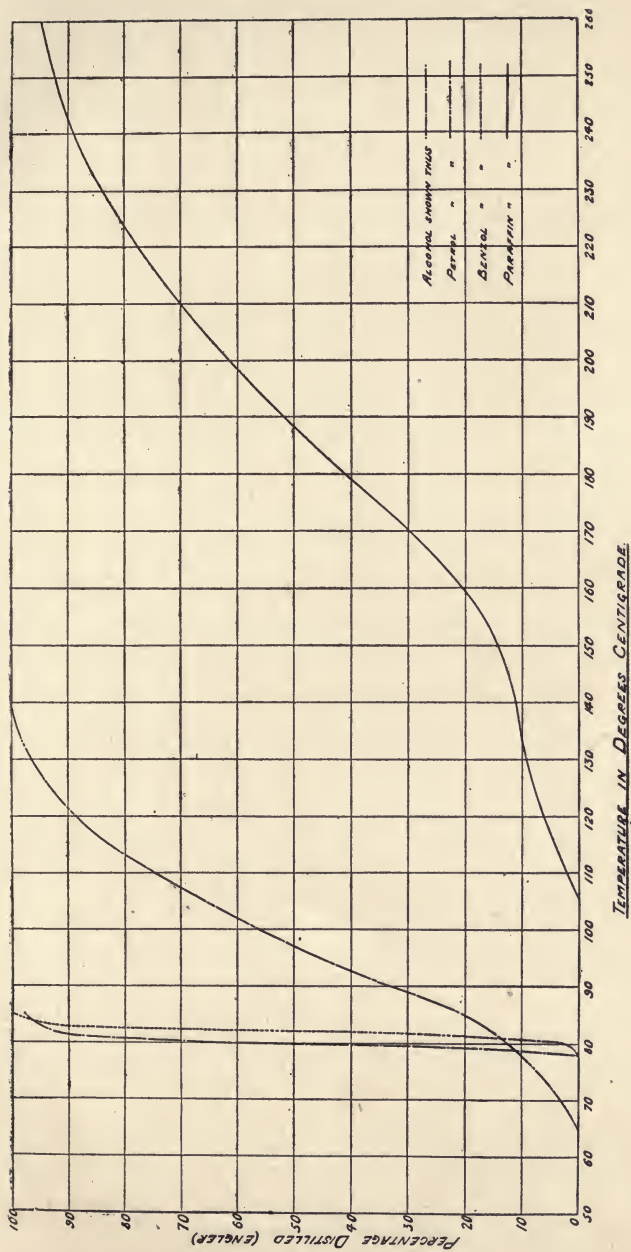


FIG. 6.

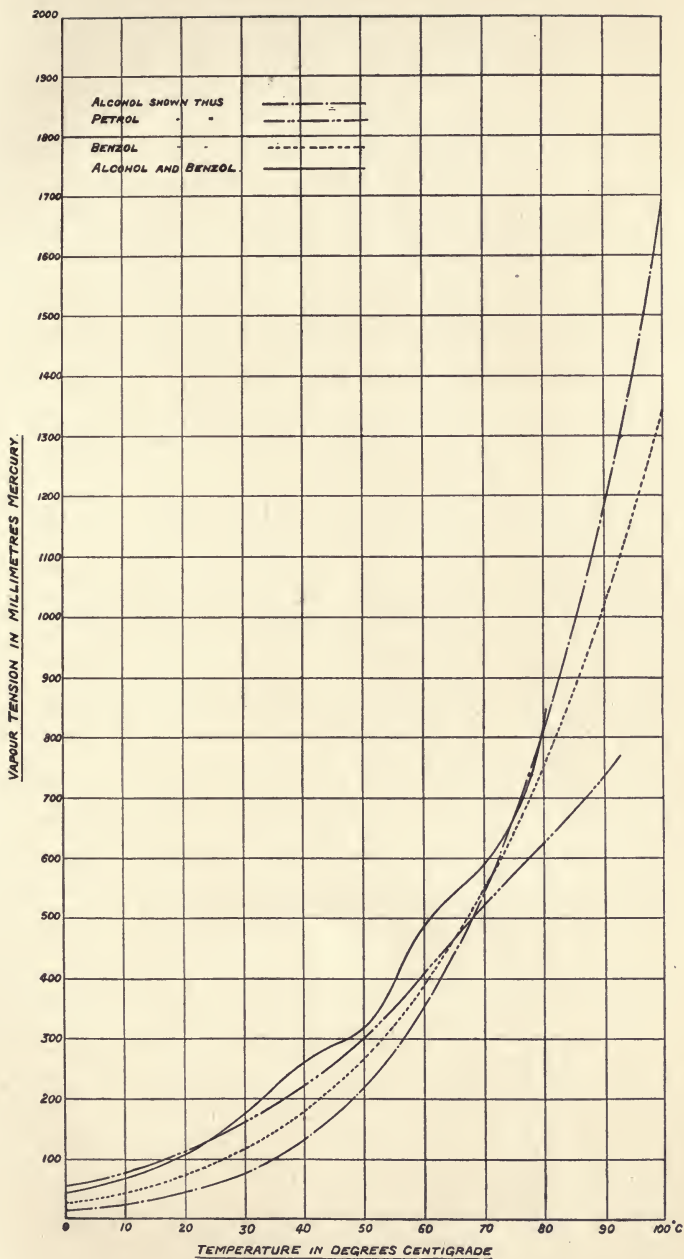


FIG. 7.

[To face page 44.]

The variation of this range for different fuels has considerable influence on their behaviour.

For petrol the explosion limits are from 1·1 to 5·3 per cent. of fuel in air ; for alcohol, 4 to 13·6 per cent. ; and for benzene, 2·7 to 6·3 per cent. Acetylene gas possesses the remarkable range of 3·2 per cent. to 52·2 per cent. A wide explosion range is naturally an advantage, as it decreases the danger of stoppage of the engine due to misfiring caused by too weak or over-rich mixtures. The range being at a higher or lower concentration can be compensated to a certain extent by correspondingly increasing or decreasing the size of jet in the carburetter. The influence of viscosity must be taken into account when experimenting with jets on various fuels.

Velocity of Flame Propagation.—The velocity of flame propagation has a considerable effect upon the adjustment and running of petrol engines. It is, however, a property which cannot be measured except by detailed research, and the figures available are meagre, and frequently will not stand comparison with results obtained from other sources. The importance of this property is shown by its influence on the degree of advance on the ignition used in all types of internal combustion engines, whether fired by electric spark, by other devices, or by spontaneous ignition, as in the Diesel engine. Assuming that the flame is propagated at an infinite speed, it would be necessary to time magnetos to fire exactly on inner dead centre, instead of firing many degrees before inner dead centre. When engines are only taking up their full load at comparatively high speed, *e.g.*, aircraft engines, it is possible to raise the compression considerably, for if preignition is liable to take place slightly before the piston reaches inner dead centre, the delay due to the time taken for the propagation of the flame will prevent the preignition becoming evident, so long as the full effect of the explosion is not felt before inner dead centre.

TEMPERATURE OF SPONTANEOUS IGNITION.—The temperature of spontaneous ignition (see p. 142) denotes the temperature to which a fuel must be raised before ignition takes place without the aid of a spark or other igniting device. This point varies for different pressures, but by comparing fuels under similar conditions the relative values may be obtained.

Holm¹ has observed this point for several bodies in

¹ Holm, *Zeits. f. angew. Chem.*, 1913, p. 273.

oxygen at atmospheric pressure, and gives amongst others the following values :—

Hydrogen	-	-	-	470° C.
Petrol	-	-	-	415° C.
Paraffin oil	-	-	-	370° C.
Paraffin wax	-	-	-	310° C.
Alcohol	-	-	-	510° C.

It will be observed that generally the higher the molecular weight of compounds of the same series the lower is the spontaneous ignition temperature. That is to say, the more complex a molecule, the less stable it is towards heat.

In experiments by Holm and by the author, it has been found that benzol and alcohol possess higher ignition temperatures than petrol. This fact has a great influence on the thermal efficiency of engines, such as the petrol engines of either two or four stroke cycle, as these compress their fuel in the working cylinder prior to the explosion. As the heat of compression and the heat of the surrounding cylinder cause a rise in the temperature of the explosive mixture, it is frequently found that ignition of the charge takes place before it is desired, *i.e.*, before the introduction of the spark. This occurrence is known as pre-ignition. It is accompanied by great loss of power, as the pressure is exerted on the piston before inner dead centre, thus tending to reverse the engine. A high compression pressure in the cylinder gives a high compression temperature, and is therefore likely to cause pre-ignition.

If the calorific power of a fuel be known, it is possible by means of Joule's equivalent to calculate the work which this amount of heat should yield. In practice we find that all types of engines only convert a comparatively small proportion of the heat into work, the larger portion being lost through radiation, circulating water, friction, temperature of the exhaust gases, and other causes. The proportion that the heat converted into work bears to the total heat introduced into the engine (or boiler, in case of steam installations) is known as the thermal efficiency.

High compression pressures tend to give high thermal efficiency, provided that pre-ignition can be avoided. The ordinary automobile engine running on petrol cannot employ a compression pressure of more than about 80 lbs., otherwise

pre-ignition takes place. With a compression of from 60 to 80 lbs. per square inch the thermal efficiency of a petrol engine is approximately 20 per cent., that is to say, one-fifth of the latent energy stored in the fuel is turned into useful work, the remaining four-fifths being lost during the process of conversion. When employing benzol an increase of compression up to 150 to 180 lbs. per square inch is admissible. Alcohol, possessing a very high ignition point, will allow the compression to be raised to about 200 lbs. per square inch, whereby a thermal efficiency of over 35 per cent. can be attained. In the Diesel engine, which works on a different cycle, the fuel is not introduced into the working cylinder until near the end of compression, a method of operation which affords no opportunity for pre-ignition to take place. The Diesel engine employs a compression pressure of about 500 lbs. per square inch, and yields a maximum of about 40 per cent. thermal efficiency, which is the highest yet obtained by any device for converting heat into work. Incidentally it may be noted that as the temperature attained in the cylinder of a Diesel engine is considerably in excess of the ignition point of the petroleum fuel oils generally used in this engine, it is unnecessary to employ any electric spark or other means of ignition, as the fuel spontaneously ignites.

From these facts it will be observed that the temperature of spontaneous ignition is a point of fundamental importance in all fuels for internal combustion engines.

CALORIFIC POWER.—The calorific power of fuels for petrol engines naturally is of primary importance, as this value represents the amount of energy available. The gross calorific power of commercial petrols recently determined by the author varies from 11,000 to 11,500 cals. (19,800 to 20,700 B.Th.U.). Samples of benzol (100 per cent. at 100° C.) and industrial mineralised alcohol gave 9,877 cals. and 6,115 cals. (17,779 and 11,007 B.Th.U.) respectively.

It will be observed that alcohol is much lower in calorific power than either petrol or benzol, but as alcohol requires less air to effect its combustion (and therefore less heat is lost to the exhaust), and will withstand a higher compression pressure, it is more efficiently converted into work than the other two fuels.

SPECIFIC GRAVITY.—The specific gravity should be taken into consideration when buying motor spirits, as it is usual to

measure them by volume, whereas heat measurements are taken on unit weight. As the heavier petroleum spirits give almost the same heat value per unit weight, they yield considerably more heat per gallon than the lighter fuels.

1 gal. of water weighs 10 lbs., therefore 1 gal. of high grade spirit, sp. gr. .700, weighs 7 lbs.: a heavier grade, sp. gr. .735, would weigh 7.35 lbs.

When valuing spirit it is therefore necessary to calculate the British thermal units per gallon.

Comparing petrol, sp. gr. .700, with a net calorific value of 18,500 B.Th.U. with a benzol, sp. gr. .880, and net calorific power 17,100 B.Th.U., we find that:—

1 gal. petrol weighing 7.00 lbs. contains $7.00 \times 18,500 = 129,500$ B.Th.U.

1 gal. benzol weighing 8.80 lbs. contains $8.80 \times 17,100 = 150,480$ B.Th.U.

Thus if the price of the two products be the same, benzol is the cheaper fuel, though it possesses a lower calorific power than petrol.

AIR REQUIRED FOR COMBUSTION.—The weight of air theoretically required for the combustion of 1 lb. of any fuel can be calculated approximately from the chemical composition of that fuel by the following formula:—

$$A = 11.6 \left[\frac{C + 3 \left(H - \frac{1}{8} O \right)}{100} \right]$$

Where A is the weight of air required in pounds,
 C „ percentage of carbon present,
 H „ „ hydrogen present,
 O „ „ oxygen present.

The quantity of air required affects the thermal efficiency, as where little air is required less of the heat is lost through the exhaust.

1 lb. of petrol requires about 15 lbs. of air to obtain theoretically complete combustion; 1 lb. of benzene requires $13\frac{1}{2}$ lbs. of air, and 1 lb. of alcohol requires $8\frac{3}{4}$ lbs. of air.

ULTIMATE COMPOSITION.—The ultimate composition shows the percentage of chemical elements which the fuel contains, and is necessary to allow of the calculation of the theoretical quantity of air required for complete combustion. It is also to some extent an indication of the likelihood of

carbon being precipitated in the cylinder, as those bodies which are richest in carbon are most likely to form deposits on the piston top, exhaust valve, and cylinder head.

The difference between the gross and net calorific powers is calculated from the hydrogen content of the fuel, which is found in the ultimate analysis. Therefore the ultimate composition has to be determined in order to ascertain the net calorific power.

Petroleum Motor Spirits.—The fractions of crude petroleum boiling up to 150° C. are worked up into products, the larger portion of which goes to form the various grades of motor spirit. Before the demand for petrol had become so large as to induce manufacturers to make use of every available portion of the products it was customary to select fractions boiling from 70° C. to about 115° C. for the motor spirit market. This temperature range has been enlarged so as to include nearly all the products obtained by the first distillation of the crude oil (up to 150° C.). In some cases higher boiling points than 150° C. are employed. The specific gravity of petrol has similarly undergone a change from '690 (in the days of surface carburetters) to '700 about 1909, and at present some varieties possess specific gravities above '740.

The boiling point of good quality petroleum motor spirit is generally from 70° C. to 130° C. The specific gravities of some commercial samples recently tested by the author were as follows, their volatility being shown by the yield of distillate by retort test at 120° C. :—

	Specific Gravity at 20° C.	Retort Test.
Pratt's perfection - -	0·706	87 per cent. at 120° C.
„ No. II. - - -	0·713	87 „ „
„ taxibus - - -	0·722	86 „ „
Mex spirit - - -	0·718	88 „ „
Meade-King, Robinson—		
Grade I. - - -	0·714	88 „ „
„ II. - - -	0·735	80 „ „
„ III. - - -	0·747	70 „ „
Benzol ("100 per cent.") -	0·875	100 „ at 100°
Alcohol (industrial) - -	0·819	100 „ 80°

The values for industrial mineralised alcohol and commercial 100 per cent. benzol (distilling 100 per cent. at 100° C.) are given for comparison.

The petrols obtained by direct distillation of Pennsylvanian and similar crude oils consist mainly of the first five liquid members of the methane series (saturated aliphatic hydrocarbons).

	Formula.	Composition.		Boiling Point.
		Carbon.	Hydrogen.	
Pentane - - - -	C_5H_{12}	83.3	16.7	37° C.
Hexane - - - -	C_6H_{14}	83.7	16.3	69° C.
Heptane - - - -	C_7H_{16}	84.0	16.0	98° C.
Octane - - - -	C_8H_{18}	84.2	15.8	125° C.
Nonane - - - -	C_9H_{20}	84.3	15.3	150° C.

The hydro-aromatic compounds found in Russian petroleum consist largely of the following hydrocarbons:—

	Formula.	Composition.		Boiling Point.
		Carbon.	Hydrogen.	
Methyl cyclo-pentane -	C_5H_{10}	85.7	14.3	71° C.
Cyclo-hexane - - -	C_6H_{12}	85.7	14.3	80° C.
Dimethyl cyclo-pentane -	C_7H_{14}	85.7	14.3	91° C.
Methyl cyclo-hexane -	C_7H_{14}	85.7	14.3	98° C.
Cyclo-heptane - - -	C_7H_{14}	85.7	14.3	100° C.
Dimethyl cyclo-hexane -	C_8H_{16}	85.7	14.3	118° C.
Cyclo-octane - - -	C_8H_{16}	85.7	14.3	119° C.

As petrol is not a pure chemical compound but a mixture of a large number of compounds, its properties cannot be definitely stated, as they vary in each different grade. The

figures shown in the following list will show the properties of any ordinary grade :—

Distillation	-	-	70° C. to 150° C.
Latent heat of vaporisation	-	-	80 cal.
Vapour tension in millimetres	-	-	78 mm. at 10° C., and 400 mm.
mercury	-	-	at 50° C.
Explosive range	-	-	1·1 to 5·3 per cent.
Temperature of spontaneous ignition in oxygen	-	-	265° C. to 280° C.
Gross calorific power	-	-	11,100 cal., 19,980 B.Th.U.
Net	„	„	10,240 cal., 18,432 B.Th.U.
Specific gravity at 15° C.	-	-	·690 to ·760.
Theoretical air required for combustion	-	-	15·2 lbs. per lb.
Elementary composition	-	-	Carbon, 84 per cent., hydrogen, 16 per cent.

Petrol has hitherto been the main fuel for carburetting engines, but during 1913 and 1914 a considerable amount of benzol found its way on to the motor spirit market.¹ Shale spirit was also used for motor fuel. The increase in the use of petroleum spirit is clearly shown by the quantities of spirit imported into the United Kingdom during recent years :—

1905	-	-	-	18,000,000 gallons.
1906	-	-	-	25,000,000 „
1907	-	-	-	34,000,000 „
1908	-	-	-	40,000,000 „
1909	-	-	-	53,000,000 „
1910	-	-	-	55,000,000 „
1911	-	-	-	70,000,000 „
1912	-	-	-	80,000,000 „
1913	-	-	-	101,000,000 „
1914	-	-	-	120,000,000 „
1915	-	-	-	144,574,891 „
1916	-	-	-	161,410,824 „
1917	-	-	-	139,270,181 „
1918	-	-	-	192,959,054 „

The increased demand has been largely met by including fractions which previously were not considered suitable for motor use.

¹ V. B. Lewes estimates the use of these substitutes at about 10,000,000 gals. in 1914 (Fothergill Lectures, Royal Society of Arts).

Not only have higher boiling fractions been adopted, but also the lower boiling distillates have been put into use. It has become common practice in the United States to condense the heavier hydrocarbons from the natural gas by means of cooling under pressure, and to mix this very volatile product with heavier grade distillates.¹ The light spirit, when used in this way, enters into solution in the heavier portion of the mixture, and acts as a "livening" agent by increasing the vapour pressure, and generating sufficient gas in the carburetter to allow the heavier portion to be burnt. The heavy fuel is partly carried over by the generation of gas from the lighter product, and the remainder is burned, owing to the atomising action of the spray in the carburetter. Such fuels find considerable use for stationary petrol engines in the United States.

By encroaching further into the kerosene fraction we obtain spirits which are low in vapour tension, which deficiency causes difficulty in the starting of the engine, and lack of "flexibility," that is, of the property of allowing wide variations in speed and load. Mixtures of petrol and kerosene can be used for motor purposes, but the higher the proportion of kerosene the greater becomes the trouble in starting, and, with automobiles, the more difficulty of control is experienced when driving in traffic, on account of slow response to the throttle. A simple mixture of this description does not therefore prove itself advantageous, except in special cases where flexibility is not required to any great extent. The use of a special tank, and in some cases a special carburetter, for starting on petrol overcomes this difficulty, but is an undesirable complication.

A great increase in the proportion of spirit yielded by the crude oil has of recent years been obtained by developments and discoveries in the process of cracking the heavier portions of the oil. The cracked spirit generally shows a slightly higher specific gravity when compared with a spirit, distilling at the same temperature, which has been obtained by simple distillation. Cracked spirit contains a greater proportion of unsaturated hydrocarbons than spirit which has been pro-

¹ See Technical Paper No. 10, U.S. Bureau of Mines.

duced by direct distillation, but as a motor fuel it has been found quite satisfactory, though somewhat unpleasant in smell. On account of its comparatively high specific gravity it contains more heat units per gallon than ordinary spirit, and therefore gives a greater mileage when used in an automobile. The cracking of petroleum residues is now conducted on a large scale in the United States, but the larger portion of the cracked product is consumed in that country, while the ordinary spirit is exported.

As both the unsaturated aliphatic hydrocarbons found in cracked spirit and the hydro-aromatic compounds (which form the greater portion of Caucasian petroleum) possess higher specific gravities than the members of the methane series which boil at corresponding temperatures, it is evident that the specific gravity is often misleading, if considered as an indication of the volatility of a motor spirit.

In view of the increasing demand for liquid fuels, and the absence of petroleum deposits in this country, many experiments have been made with the object of finding a method of producing a liquid fuel similar to petroleum from coal. The most successful results have been obtained by the low temperature destructive distillation of suitable coals (particularly cannel coal). By low temperature carbonisation in partial vacuum, or under other conditions which ensure the rapid removal of the volatile products, it is possible to obtain tars rich in aliphatic hydrocarbons, and which in many respects resemble crude petroleum. The lower boiling fractions obtained by the distillation of such coal tars are akin to petrol, and after refining may be used in carburetter engines, when they are hardly distinguishable from the petroleum product. The low temperature carbonisation of coal has not yet been conducted on a sufficiently large scale to allow of the products being placed upon the motor spirit market, but developments along these lines may be expected in the near future.

Benzene.—When the price of petrol commenced to rise rapidly, owing largely to the shortage of motor spirit, the first substance to receive attention as a possible alternative fuel was benzene.

Benzene is an aromatic hydrocarbon of the formula

C_6H_6 , and is obtained from the products of the destructive distillation of coal.

The pure hydrocarbon possesses the following properties :—

Boiling point	-	-	-	-	80·4° C.
Latent heat of vaporisation	-	-	-	-	93·7 cal.
Vapour tension, 45·4 mm. mercury at 10° C.,	-	-	-	-	74·66 mm. at 20° C.
Explosive range	-	-	-	-	2·7 per cent. to 6·3 per cent.
Temperature of spontaneous ignition in oxygen	-	-	-	-	566° C. ¹
Gross calorific power, about 10,050 cal. =	-	-	-	-	18,090 B.Th.U.
Specific gravity at 15° C.	-	-	-	-	·88.
Theoretical air required for combustion	-	-	-	-	13·46 lbs. per lb.
Elementary composition, 7·7 hydrogen, 92·3 per cent. carbon.	-	-	-	-	

The pure hydrocarbon benzene is never used on account of its high price and comparatively high freezing point (+6° C.). Commercial benzol containing 70 to 80 per cent. of benzene is much lower in freezing point, and is a cheaper product. Although the calorific power of benzol is below that of petrol, it gives a greater quantity of heat per unit of volume on account of its higher specific gravity. It is found in practice that from 12 to 15 per cent. greater mileage is obtained from benzol than from an equal volume of petrol, when the compression pressure of the engine is suited for petrol.

In all respects benzol has been found to give satisfaction in automobile engines, in which it can be used without any modification of existing arrangements beyond a slight adjustment of the float level in the carburetter.

It is possible to employ compression pressures of 150 to 180 lbs. per square inch in carburetter engines when running on benzol. This increase in compression greatly improves the efficiency of the engine, and gives benzol a further advantage over petrol. If the compression of an engine is so increased, it makes the engine unsuitable for use with petrol, and on this account it is usual to employ benzol on petrol engines with normal compressions (70 to 90 lbs. per square inch) whereby a lower efficiency is obtained, but the engine is capable of running on either fuel.

Commercial benzol, such as is used for motor purposes in this country, is a product of which 90 per cent. distils at

¹ 100 per cent. benzol ; figure determined in author's instrument.

100° C., or 100 per cent. at 100° C., and is known as 90 per cent. benzol or 100 per cent. benzol. The 90 per cent. benzol contains approximately 70 per cent. of benzene, 30 per cent. of toluene, and traces of xylenes.

The adoption of benzol would undoubtedly have solved the motor spirit problem if only sufficient of the product had been available. Benzol is produced on a large scale from two sources, namely, by the distillation of coal tar, and by "stripping" coke oven gas. Gray and Mellanby¹ estimate the possible yield of suitable motor spirit from coal tar as 1½ to 2 million gallons per annum. The actual production from this source is probably even less.

The greater portion of the benzol produced in the destructive distillation of coal remains in the gas. In the manufacture of coal gas it is not profitable to remove this product, on account of its high luminosity. Coke oven gas is, however, not required to possess high luminosity, and the benzol is therefore removed. By calculation of the coal used for the preparation of metallurgical coke, and assuming the entire quantity of benzol recovered from the gas at 1·54 gals. per ton of coal, Gray and Mellanby² estimate the possible production of 90 per cent. benzol from coke oven gas at 26 million gallons, and the actual production in the neighbourhood of 11 million gallons.

Probably, at the present time, if all the coke oven gas were stripped, the yield from this source would be approximately 40,000,000 gallons, but there is extreme difficulty in getting reliable statistics.

During 1914 the petrol imported into this country amounted to 120 million gallons.

During the war, Government regulations enforced the extraction of benzol and toluol from illuminating gas, but this practice has not been general in normal times.

As the yield of toluene in both gas and tar is much smaller than that of benzol, there is but little probability of it being used alone, or being added to benzene in greater quantities than are present in the commercial 90 per cent. benzol.

¹ "Fuel Oils, and their Application to the Generation of Power." Paper presented to Institution of Engineers and Shipbuilders in Scotland.

² *Ibid.*

Alcohol.—Ethyl alcohol differs greatly from petrol and benzol in that it is not a hydrocarbon, but contains a large proportion of oxygen.

The more important properties of pure ethyl alcohol as a fuel are given in the following list:—

Boiling point	-	-	78.4° C.
Latent heat of vaporisation	-	-	203 cal.
Vapour tension	-	-	41.3 mm. at 18.7°; 766.5 mm. at 78.5° C.
Explosive range	-	-	4 per cent. to 13.6 per cent.
Temperature of spontaneous ignition in oxygen	-	-	395° C. ¹
Gross calorific power	-	-	7,054 cal. = 12,697 B.Th.U.
Specific gravity	-	-	.800.
Theoretical air required for combustion	-	-	9.08 lbs. per lb. fuel.
Elementary composition—carbon, 52.17 per cent.; hydrogen, 13.04 per cent.; oxygen, 34.78 per cent.			

Pure ethyl alcohol is expensive and difficult to prepare, but a solution of from 90 to 95 per cent. alcohol (the remainder being water) can easily be obtained by distillation. There are at present available such grades of spirit as "industrial mineralised spirit," and "methylated spirit," but these are too expensive to use as motor fuel. A sample of the former on examination was found to have a specific gravity of 0.819 at 20° C., and a gross calorific power of 6,115 cal. (11,007 B.Th.U.).

Though very low in calorific power, alcohol possesses several properties which make it exceptionally suitable for use in internal combustion engines.

The high temperature of spontaneous ignition (395° C.) allows the use of high compression pressures without pre-ignition taking place. Whereas petrol (ignition temperature about 270° C.) can only be used with a compression pressure of 70 to 90 lbs. per square inch, with alcohol the compression pressure can be raised to 200 lbs. per square inch. By this means the thermal efficiency may be increased from 22 per cent. to over 30 per cent. Alcohol possesses a higher specific

¹ Mineralised spirit, sp. gr. .819: figure determined in the author's instrument.

gravity than petrol, weighing about 8.2 lbs. per gallon, against petrol at 7.2 lbs. per gallon, this fact being favourable to alcohol when bought by volume measure. Alcohol requires a less quantity of air for its combustion, which decreases the proportion of heat passing to the exhaust.

It is found in practice that, provided the compression of the engine is raised, alcohol will yield very nearly the same power per unit volume as petrol. Also an engine of given capacity will generate more power from alcohol than from petrol.¹

Although the expense of manufacturing alcohol, together with the Government restrictions on its use, have hitherto prevented its employment in engines in this country, it has met with success as a fuel on a commercial scale in France and Germany, and experiments have been conducted on a large scale in the United States with a view to its employment.

Alcohol is the only fuel which can be prepared without drawing on existing natural stores, and there is therefore no limit to the amount available. If its use should meet with success it therefore might prove a final solution to the motor spirit problem.

The liability of alcohol to oxidation, with the formation of acetaldehyde and acetic acid, has not been found to cause much trouble in practice. The low vapour pressure, together with the comparatively large proportion of fuel required to form an inflammable mixture, makes it difficult to start engines on alcohol. This trouble may be overcome by employing a mixture of alcohol and petrol, or alcohol and benzol, or by starting and running on petrol or benzol until the engine is warm.

On account of the elementary composition of alcohol it is possible to obtain a greater power by the use of an excess of fuel, accompanied by incomplete combustion, than by using the theoretically correct mixture. According to Watson and others, who have gone very fully into the use of alcohol as a fuel, we learn that "the mean effective pressures obtained with alcohol were very slightly higher than those obtained

¹ United States Geological Survey, Bulletin 392, 1909.

with either petrol or benzol, while they increased more rapidly with the strength of mixture than was the case with either of the other fuels, so that even with the strongest mixture used (six of air to one of alcohol), which gave 6 per cent. of carbon monoxide in the exhaust, the mean effective pressure still showed a sign of increasing with the strength of the mixture. This is a point which may be of some practical importance, as if, as is ordinarily the case, the carburetter is adjusted to give approximately maximum power, there will be a very appreciable loss due to incomplete combustion."¹

As it is required by law that fuel alcohol be rendered unsuitable for drinking by the addition of some highly disagreeably tasting substance, such as pyridine or wood spirit, it is necessary to consider the effect of such denaturants upon the fuel properties of the mixture.

The cost of denaturing spirit, together with the inconvenience of other Government regulations regarding its production, are sufficient to prevent the use of alcohol as a fuel in this country at present. The denaturants at present permissible are unsuitable for use in engines.

It has been suggested² that benzol should be allowed as a denaturant. Certainly many cheap and non-injurious denaturants would be available provided that the excise regulations were modified.

Fuel Mixtures for Petrol Engines.—Many mixtures have been suggested for use as motor spirits, and a large number of these have been patented. There have been during the war a large number of "petrol substitutes" on the market, but the majority of these were poor in quality, and show that the problem had not been properly understood by the makers.

The preparation of suitable mixtures must depend upon the properties of the ingredients, which should be blended so as to yield a final product possessing all the properties requisite for a carburetter engine fuel.

¹ Extract from paper read before the Institute of Automobile Engineers, 9th December 1914.

² Motor Union Fuel Committee Report.

The more important substances which are available for making motor spirit mixtures are as follows :—

Petrol, or similar low boiling petroleum products.

Kerosene, or other petroleum fractions boiling between 150° C. and 300° C.

Benzene and benzol.

Toluol, xylols, solvent naphtha, and coal tar distillates boiling up to 200° C.

Turpentine and wood spirits.

Naphthalene.

Alcohol.

Ether.

Acetone.

Condensed natural gas and petroleum distillates boiling below 60° C.

Acetylene.

Oxidising agents.

There is no reason why many other substances should not be employed.

Kerosene and the heavier coal tar products are the cheapest liquids available, and therefore are suitable for constituting the bases of fuel mixtures. They are, however, not sufficiently high in vapour pressure, and therefore highly volatile liquids or solutions of gases must be added before they can be made sufficiently volatile to allow an engine to start from cold.

By adding to kerosene condensed natural gas, or the exceedingly volatile hydrocarbons which are produced in the earlier stages of petroleum distillation, a mixture possessing most of the properties of petrol may be obtained. Such mixtures will start from cold without difficulty, and are in common use in the United States.

A mixture is suggested by Lewes¹ consisting of 50 per cent. kerosene distilled up to 250° C.; 40 per cent. petrol, specific gravity about 720; and 10 per cent. benzol.

By blowing acetylene into benzol a solution of high vapour tension is obtained. This may be mixed with about twice the quantity of kerosene, and yields a mixture which is said to keep

¹ V. B. Lewes, Fothergill Lectures, Royal Society of Arts.

almost indefinitely, and which, when used in a petrol engine, will give no difficulty in starting.

Acetylene is also soluble in alcohol (6 vols.), and in acetone (24 vols.), and such solutions may be employed as "livening" agents, to be added to fuels deficient in volatility.

In order to obtain a high efficiency from alcohol, it is necessary to increase the compression of the engine. This necessitates dismantling, and a considerable amount of work. If alcohol is to be consumed in an ordinary petrol engine without special modifications, it is most economical to consume it in the form of a mixture.¹

Alcohol is exceedingly low in carbon content, and it is therefore possible to add naphthalene, which is rich in carbon, without risk of carbon deposits being formed in the engine. Mixtures of a solution of naphthalene in alcohol and kerosene are cheap and effective, and have been used in large quantities in Germany, both before and during the war.²

Naphthalene (see p. 26) has been used as a constituent of many motor spirit mixtures, and is said to be capable of yielding a vapour-air mixture suitable for internal combustion engine use without any addition of other products, if this fuel is melted and all pipes kept warm.³

The accompanying table shows the solubility of naphthalene in one hundred parts of various solvents :—

Solvent.	Solubility in 100 Parts of Solvent at	
	10° C.	0° C.
Alcohol - - - -	5.00 parts	4.25 parts
Petroleum ether - -	11.05 "	7.75 "
Benzene - - - -	40.70 "	32.00 "
Toluene - - - -	35.30 "	24.80 "
Xylene - - - -	29.00 "	20.80 "

¹ At the time of writing, extensive trials are being conducted in London on the motor-bus services on alcohol-benzol mixtures.

² Alcohol is not soluble in benzene or kerosene unless the concentration of the alcohol is about 97 per cent., and researches are being conducted at present to find methods of obtaining such mixtures in solution. Fusel oil, it is claimed, assists the solution of alcohol in benzol.

³ H. K. Bruhn, *Journ. f. Gasbeleuchtung*, 2nd and 9th November 1915.

The heavy coal tar distillates have been employed as bases for motor spirit. The nature of the mixture has not been made public, but successful trials of at least one such fuel have been made. Solvent naphtha is to the author's knowledge the heaviest coal tar fraction which has been utilised in the manufacture of motor spirit.

Small quantities of ammonia have been added to mixtures containing alcohol, the object evidently being to neutralise any acid formed by the oxidation of the alcohol before its entry into the engine. A fuel mixture known by the trade name of "natalite" is said¹ to consist of 40 per cent. ether and 60 per cent. rectified alcohol (prepared from molasses), traces of ammonia being present. The journal, *The Engineer*, carried out tests on this fuel, and found the consumption in an automobile engine to be approximately the same as with petrol. A reduction of the air supply was found to be necessary.

The advantage of employing picric acid, ammonium perchlorate, and hydrogen peroxide as additions to motor spirits is doubtful. It has been claimed that they increase the speed of the explosion, and also that they assist the combustion of heavier fuels.

The preparation of mixtures for use as motor spirit is a subject which is yet but in its infancy, and future research may be expected to yield many interesting results.

¹ *Chem. Trades Journal*, 19th June 1915.

CHAPTER IX

FUELS FOR ENGINES FITTED WITH VAPORISERS

UNDER the term of "Engines Fitted with Vaporisers" will be considered only engines in which the fuel enters the cylinder before the compression stroke. Engines in which the fuel is vaporised in a heated chamber, and admitted to the cylinder at the end of compression, are being classed in the section dealing with engines fitted with atomisers.

Vaporisers have the object of enabling engines working on the same principle as the petrol engine (either two-stroke cycle or four-stroke cycle) to work on heavier fuels than is possible with a carburetter. In order to overcome the difficulties caused by low vapour tensions, it is necessary to employ some means of heating the fuel. The heat may be provided either from the engine exhaust, from circulating water, or by special heating arrangements separate from the engine. When vaporisers obtain their heat from the engine it is necessary to employ special heating arrangements for starting, or to start on petrol, and to run on this until the engine is warm. Engines fitted with vaporisers are usually intended to run on kerosene (paraffin oil or lamp oil) prepared either from petroleum or from shale oil. They are also suitable for consuming alcohol, which yields greater satisfaction when used in a vaporiser than when a carburetter is employed. In either case a preliminary heating, either by special means or by running on petrol, is necessary. Engines intended solely for use with alcohol are adjusted so as to give higher compression pressures than ordinary paraffin engines.

The kerosene fraction forms a larger proportion of the crude oil than the petrol fraction, therefore the heavier fuel is available in larger quantities. On account of its use as

an illuminant, kerosene is obtainable in most parts of the civilised world, and its high flash point makes it safer and cheaper to handle and store than petrol. Though the calorific power of kerosene is slightly lower than that of petrol, this difference is more than counterbalanced by its higher specific gravity. For example, a kerosene of specific gravity $\cdot 800$ possesses a gross calorific power of 20,100 B.Th.U., therefore one gallon will yield $8 \times 20,100 = 160,800$ B.Th.U. A petrol of specific gravity $\cdot 710$ possesses a gross calorific power of 20,500 B.Th.U., therefore one gallon will yield $7 \cdot 1 \times 20,500 = 145,500$ B.Th.U.

The power available from kerosene is therefore greater by about 12 per cent. than that which is obtainable from an equal volume of petrol. When kerosene was obtainable at less than half the price of petrol, there was a great economy in substituting it for petrol wherever possible. At the present time the advantage is not so marked. Vaporiser engines are used for a great variety of purposes, and are especially suitable for the propulsion of small boats (launches, fishing craft, barges, etc.), and for small land installations.

Kerosene is the fraction collected between 150° and 300° C. during the first distillation of crude petroleum. It is a mobile, transparent, and almost colourless liquid. Analyses of several samples of kerosene and heavier distillates (solar oils) are shown in the two accompanying tables:—

COMPOSITION AND CALORIFIC VALUES OF PARAFFIN OILS.¹

Name.	Specific Gravity.	Composition.			Calories per Kilo.	Calorific Value.	
		Carbon.	Hydrogen.	Oxygen, Nitrogen, Etc.		B.Th.U. per Pound.	B.Th.U. per Gallon.
Royal Daylight (American)	0·797	85·70	14·20	...	11,167	20,100	158,000
Kerosene (American)	0·780	85·05	14·40	0·55	11,163	20,095	156,500
Refined (Baku) -	0·825	86·00	14·00	...	11,270	20,300	167,000
Russele R.V.O. -	0·890	85·95	13·50	0·45	10,901	19,620	174,500
Solar oil -	0·896	86·61	12·60	0·79	10,783	19,450	174,000

¹ W. Inchley, *The Engineer*, 1911, iii., p. 155.

PETROLITE BY VACUUM OIL CO.

Specific gravity - - - 814 at 20° C.

Retort Test.
(Bulb of Thermometer
Immersed.)

Engler Flask Distillation.

Drop at 190° C.

Drop at 137° C.

7 per cent. at 200° C.

22½ per cent. at 200° C.

53 " 250° C.

63 " 250° C.

75 " 275° C.

95 " 300° C.

96 " 300° C.

Gross calorific value - 11,020 cals. = 19,836 B.Th.U.

Net " " - 10,294 " = 18,529 "

Viscosity (Redwood) - 5.00 units at 70° F. { standard : rape
oil = 100 units
at 60° F.

Closed flash point (Gray) - - - 104° F.

Water - - - - - None.

Ash - - - - - None.

Coke - - - - - None.

Spontaneous ignition temperature in oxygen - 251.5° C.

Special distillates are frequently prepared for use in vaporising engines; such products are often slightly lower in specific gravity and in boiling point than illuminating oils. A sample of a shale product, "Oil-Engine Oil," from the Broxburn Oil Co., recently examined by the author, yielded the following analysis:—

Specific gravity - - - 768 at 20° C.

Distillation from Engler Flask.

Drop at 140° C.

72 per cent. at 180° C.

12 per cent. at 150° C.

82 " 190° C.

24 " 160° C.

88 " 200° C.

55 " 170° C.

Gross calorific value - 11,250 cals. = 20,250 B.Th.U.

Net " " - 10,485 " = 18,873 "

Viscosity (Redwood) - 4.2 units at 70° F. { standard : rape
oil = 100 units
at 60° F.

Closed flash point (Gray) - - - 86° F.

Asphaltum- - - - - None.

Water - - - - - None.

Sulphur - - - - - 0.15 per cent.

Ash - - - - - None.

Coke - - - - - 0.31 per cent.

Mechanical impurities - - - None.

Spontaneous ignition temperature in oxygen 253° C.

As the spontaneous ignition temperatures of kerosenes are generally lower than these values for petrols, it is necessary to employ slightly lower compressions in engines running on the former fuels. Russian kerosenes (which are rich in hydro-aromatic hydrocarbons) are said to withstand slightly higher compressions than the American oils.¹

The use of oils other than distillates on simple vaporising engines is rare, and such oils will therefore not be treated as fuels for this type of engine.

Refined naphthalene has found use alone and more commonly as a constituent of mixtures for internal combustion engines. It is, in normal times, comparatively cheap, and possesses a high heat value. In order to obtain satisfactory results with mixed fuels rich in naphthalene, it is necessary to employ some form of vaporiser.

The following relative consumptions per B.H.P. hour of petrol, benzol, and naphthalene have been given by Bruhn :—²

Fuel.	Half Load Consumption.	Three-Quarter Load Consumption.	Full Load Consumption.
Petrol - -	16·6 oz.	13·1 oz.	11·3 oz.
Benzol - -	14·1 „	10·6 „	9·5 „
Naphthalene -	13·4 „	11·3 „	10·2 „

¹ Brame, "Fuel—Solid, Liquid, and Gaseous," p. 171.

² H. K. Bruhn, *Journ. f. Gasbeleuchtung*, 2nd and 9th November 1915.

CHAPTER X

FUEL OILS FOR ENGINES FITTED WITH ATOMISERS

UNDER "Fuels for Engines Fitted with Atomisers" are treated fuels for engines which are provided with some atomising device, and in which the fuel is forced into the working cylinder about the end of compression. The engines of this type may be roughly divided into the two classes, Diesel engines and semi-Diesel engines. There are no strict boundaries to the use of either of these terms, but for purposes of classification engines which possess no ignition appliances for either starting or running will be considered as Diesel engines. The majority of the semi-Diesel engines possess hot bulbs or some heated part so arranged as to ignite the oil charge, and these generally require heating by external means before starting the engine. Engines of both these types may operate either on the two-stroke cycle or on the four-stroke cycle.

The Diesel engine possesses several peculiar features; the fuel is injected into the cylinder near the end of compression (slightly in advance of inner dead centre), by means of a high pressure pump.

Generally, highly compressed air (500 to 1,000 lbs. per square inch) is blown in along with the oil, the air aiding in the atomisation, and to some extent helping the combustion of the fuel.

The absence of fuel in the cylinder during compression makes pre-ignition impossible, therefore high compressions (450 to 550 lbs. per square inch), may be used, by means of which a high thermal efficiency is obtained.

No ignition device is required, as the temperature attained in the cylinder is sufficiently high to ensure regular spontaneous ignition with the majority of fuels. The injection of fuel is

so arranged that there is no explosion, but instead, a period of burning continuing while the piston travels approximately one-tenth of its path on the working stroke. This arrangement results in a period of constant pressure, yielding a flat-topped indicator diagram (see Fig. 8). The thermal efficiency of the Diesel engine is higher than that of any other prime mover, often exceeding 35 per cent. With a heavy petroleum distillate, crude oil, or a petroleum residuum the consumption per B.H.P. hour at full load should lie between .40 and .46 lb.

There is no strict line of division between Diesel and

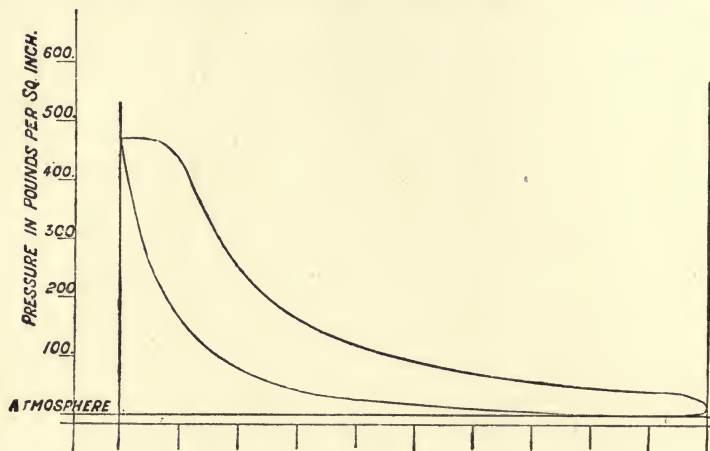


FIG. 8.—Indicator Diagram of Diesel Engine.

semi-Diesel engines, but the following remarks generally apply. The semi-Diesel engine injects its fuel at the end of compression, but usually relies on some device for igniting the fuel. The oil is injected through some type of atomiser, but without the use of compressed air. The compression pressures employed in semi-Diesel engines are lower than those of the Diesel engine, and the latter are generally built in larger sizes than the former. The semi-Diesel engine sometimes yields flat-topped indicator diagrams. As a general rule the semi-Diesel engine requires a cleaner and lighter fuel than the Diesel engine, though many manufacturers of this type of engine undertake to run on some

of the more asphaltic petroleum fuels, and in many cases the engines are claimed to work satisfactorily on tar oils. The thermal efficiency of the semi-Diesel engine is usually slightly lower than that of the Diesel engine.

Almost all classes of oils are suitable for use on Diesel and semi-Diesel engines. They will run on motor spirits, lamp oil, heavy distillates, crude oils, and residue from petroleum, but it is naturally only the cheaper of these that find general application.

The usual fuels for atomising engines are :—

Petroleum Oils.—Heavy distillates, solar and gas oils, crude oils, residua.

Shale Oils.—Crude shale oil and heavy distillates.

Lignite Oils.—Raw lignite tar and the heavier lignite tar distillates.

Oils Derived from Coal.—Certain types of raw tars, and all heavier distillates. Sometimes crude naphthalene.

Animal and vegetable oils are seldom used on account of their scarcity and high price.

Petroleum Oils.—The distillates of petroleum are, without exception, suitable for use in atomising engines, but the lighter distillates are seldom employed on account of their comparatively high price.

Kerosene is occasionally used as an ignition oil when tar oil is being consumed on Diesel engines (see p. 83).

Solar oil and gas oil are heavy petroleum distillates which are used in large quantities in Diesel and semi-Diesel engines, particularly in the latter type of engine. They are products obtained by continuing the distillation after the kerosene fraction (150° to 300° C.) has been collected. Gas oil is used in large quantities by gas works (for the manufacture of carburetted water gas or oil gas), and therefore stocks of this fuel are available in normal times in all parts of the country. Both gas oils and solar oils possess high calorific powers (over 18,000 B.Th.U. net), and on account of their freedom from water, ash, and asphaltum, they form ideal fuels, but are more expensive in preparation than the residual oils.

A sample analysis of a gas oil is as follows :—

GAS OIL FROM ANGLO-AMERICAN OIL CO.

Specific gravity - - - 850 at 20° C.

Retort Test. (Bulb of Thermometer Immersed.)

Drop at 260° C.

32 per cent. at 300° C.

60 „ 320° C.

Ignition point in oxygen	-	-	-	254° C.
Gross calorific value	-	10,880	cal.	= 19,584 B.Th.U.
Net „ „	-	10,193	„	= 18,347 „
Closed flash point (Gray)	-	-	-	184° F.
Water	-	-	-	None.
Carbon	-	-	-	85.9 per cent.
Hydrogen	-	-	-	12.8 „
Oxygen and nitrogen	-	-	-	1.09 „
Sulphur	-	-	-	0.21 „
Ash	-	-	-	None.
Coke	-	-	-	0.35 per cent.

The crude petroleum oils are seldom imported into this country, as their low flash points make them dangerous to handle, and also because it is more economical and profitable to extract the lighter portions before placing them on the fuel oil market. In the colonies and in less developed countries, where crude petroleum is found, it is common to employ the oil as fuel in the crude state, thus saving the cost of transport to and from a refinery. Crude petroleum requires careful examination before it can be considered suitable for internal combustion engine use. It often contains water, sand, leaves and similar mechanical impurities, and generally possesses a low flash point.

Crude petroleum may require filtering or settling in order to remove mechanical impurities or water before it is suitable for engine use. Crude oils and petroleum residua may be roughly divided into three categories for the purpose of classifying their properties :—

1. Paraffin base oils, *e.g.*, Pennsylvania and Ohio oils.

2. Asphaltic base oils, *e.g.*, Californian, Mexican and most South American oils.

3. Russian oils.

The paraffin base oils are generally mobile, brown or blue in colour, of low specific gravity, and comparatively rich in petrol and kerosene. Such crude oils and their residua are generally suitable for atomising engines. Paraffin base oils command higher prices than asphaltic oils.

Asphaltic oils are black, of high gravity, poor in petrol and kerosene, and vary in viscosity according to their asphaltum content. With a soft asphaltum content of from 40 to 50 per cent. they are almost solid. Such oils are not generally satisfactory for use on semi-Diesel engines, but several makers of this type of engine claim to burn them successfully. Even in a Diesel engine highly asphaltic oils are not desirable, as, unless all the conditions are entirely favourable, which is not the case with the majority of engines, there is a danger of coke being formed on the piston and exhaust valves, which necessitates frequent cleaning. Oils containing less than 10 per cent. of soft asphaltum give general satisfaction in Diesel engines, but above this figure the oils are liable to cause trouble. It is *possible* to run engines on oil with a very high asphaltum content. The author has run frequent trials on oils containing as much as 40 per cent. asphaltum, but does not consider that such fuels will give satisfaction in everyday usage.

The Russian oils, although chemically different, are very similar in their fuel properties to the paraffin base oils. For commercial purposes paraffin base and Russian oils, both crude and residua, can be closely valued from determinations of the following properties: specific gravity, coke value, water content, ash, flash point, and calorific value. The crude oils and residua of non-asphaltic origin which are sold as fuel oils in this country generally possess gravities of .850 to .890, and net calorific power about 18,000 B.Th.U. Water should be less than 2 per cent., and ash less than 0.05 per cent. The coke value should not exceed 5 per cent.

Analyses of a few non-asphaltic petroleum oils are given herewith:—

LIQUID FUELS

DIGBOI OIL FROM ASSAM.

Specific gravity	-	-	-	·890 at 20° C.
Retort Test.				
(Bulb of Thermometer Immersed.)	Engler Flask Distillation.			
Drop at 282° C.	Drop at 215° C.			
5 per cent. at 300° C.	5 per cent. at 250° C.			
25 " 350° C.	20	"	300° C.	
60 " 400° C.	45	"	350° C.	
	80	"	400° C.	
Ignition point in oxygen	-	-	-	261° C.
Gross calorific value	-	10,312 cal.	= 18,562 B.Th.U.	
Net " "	-	9,664 "	= 17,395 "	
Viscosity (Redwood)	-	14·0 units at 70° F.	standard : rape oil = 100 units at 60° F.	
" " "	-	9·1 " 100° F.		
" " "	-	5·1 " 200° F.		
Closed flash point (Gray)	-	-	-	150° F.
Asphaltum	-	-	-	None.
Water	-	-	-	Traces.
Carbon	-	-	-	86·44 per cent.
Hydrogen	-	-	-	11·68 "
Oxygen and nitrogen	-	-	-	1·72 "
Sulphur	-	-	-	0·13 "
Ash	-	-	-	0·032 "

ANGLO-AMERICAN OIL CO.'S FUEL OIL.

Specific gravity	-	-	-	·8887 at 20° C.
Retort Test.				
(Bulb of Thermometer Immersed.)				
Drop at 320° C.	63 per cent. at 400° C.			
17 per cent. at 350° C.	75	"	420° C.	
Ignition point in oxygen	-	-	-	269° C.
Gross calorific value	-	10,780 cal.	= 19,404 B.Th.U.	
Net " "	-	10,108 "	= 18,194 "	
Closed flash point (Gray)	-	-	-	236° F.
Asphaltum	-	-	-	1·54 per cent.
Water	-	-	-	None.
Carbon	-	-	-	86·7 per cent.
Hydrogen	-	-	-	12·55 "
Oxygen and nitrogen	-	-	-	0·115 "
Sulphur	-	-	-	0·635 "
Ash	-	-	-	Traces.

OIL FROM BORNEO.

Specific gravity	-	-	-	·939 at 20° C.
Retort Test. (Bulb of Thermometer Immersed.)				Engler Flask Distillation.
Drop at 295° C.				Drop at 250° C.
2 per cent. at 300° C.				24 per cent. at 300° C.
30 " 350° C.				49½ " 350° C.
54 " 400° C.				81 " 400° C.
62 " 410° C.				
Ignition point in oxygen	-	-	-	269° C.
Gross calorific value	-	10,360 cal.	=	18,648 B.Th.U.
Net " "	-	9,712 "	=	17,482 "
Viscosity (Redwood)	-	63·2 units at 70° F.	{	standard : rape
" "	-	23·1 " 100° F.		oil = 100 units
" "	-	6·7 " 200° F.		at 60° F.
Closed flash point (Gray)	-			Below normal temperature.
Asphaltum	-	-	-	1·75 per cent.
Water	-	-	-	0·25 "
Carbon	-	-	-	88·32 "
Hydrogen	-	-	-	11·26 "
Oxygen and nitrogen	-	-	-	0·072 "
Sulphur	-	-	-	0·098 "
Ash	-	-	-	Traces only.

ANGLO-PERSIAN OIL CO.'S OIL.

Specific gravity	-	-	-	·894 at 20° C.
Retort Test. (Bulb of Thermometer Immersed.)				Engler Flask Distillation.
Drop at 270° C.				Drop at 225° C.
8 per cent. at 300° C.				3 per cent. at 250° C.
25 " 350° C.				24 " 300° C.
44 " 400° C.				45 " 350° C.
55 " 420° C.				79 " 400° C.
Ignition point in oxygen	-	-	-	254° C.
Gross calorific value	-	10,550 cal.	=	18,990 B.Th.U.
Net " "	-	9,902 "	=	17,824 "
Viscosity (Redwood)	-	46·5 units at 70° F.	{	standard : rape
" "	-	15·7 " 100° F.		oil = 100 units
" "	-	6·9 " 200° F.		at 60° F.

ANGLO-PERSIAN OIL CO.'S OIL—*continued*.

Closed flash point (Gray)	-	-	-	-	200° F.
Asphaltum	-	-	-	-	7·6 per cent.
Water	-	-	-	-	None present.
Carbon	-	-	-	-	86·68 per cent.
Hydrogen	-	-	-	-	11·70 „
Oxygen and nitrogen	-	-	-	-	0·128 „
Sulphur	-	-	-	-	1·48 „
Ash	-	-	-	-	0·012 „

Asphaltic crude oils and residua are more frequently accompanied by ash and water than other petroleum oils, as their higher specific gravity and higher viscosity hinders the settling out of these impurities. Asphaltic oils are also generally high in sulphur content. At one time it was thought that sulphur affected the engines, but this view is certainly erroneous. It is probable that the deleterious effects of asphaltum, when not burned under favourable conditions, have been thought to be the action of sulphur. In samples of soft asphaltum, which have been prepared and examined by the author, the sulphur content has been between 4 and 5 per cent. If burned under favourable conditions, asphaltic oils will cause no difficulty, but unless the combustion is complete the exhaust valves will suffer. Deposits on the piston top and atomising devices are common with asphaltic oils. On no account should engines be allowed to smoke at the exhaust, as this is a sign of incomplete combustion, and the working parts of an engine may become badly carbonised in a short period under such conditions.

The difficulties experienced in burning asphaltic oils are in the author's opinion mainly caused by the following points:—

1. Asphaltum is generally present in viscous oils, which when passed through atomisers designed for more mobile fuels, are not effectually atomised, thus causing slow burning, formation of coke and smoking at exhaust.
2. Asphaltic oils, on account of their high gravity and high viscosity, are liable to hold water and mechanical

impurities in suspension. The water causes irregular burning, and the mechanical impurities affect the exhaust valve.

3. The proportion of hydrogen present in asphaltum is lower than in ordinary oils, which tends to give a smoky flame when burning.
4. Asphaltum will not distil, and on heating cokes instead of evaporating. This coke will not burn sufficiently fast to allow of complete combustion before the opening of the exhaust valve. Particles of incandescent coke heat the exhaust valve, and attach themselves between the exhaust valve face and the seat, causing injury to these surfaces. The fact that high exhaust temperatures often accompany the burning of asphaltic oils, supports this latter theory.

Heating the fuel before its entry into the engine will overcome the difficulties caused by the high viscosities of asphaltic oils, and when heat is applied to the fuel tanks for prolonged periods, it assists in the separation of mechanical impurities and water.

For most practical purposes, the asphaltic oils can be valued from an examination of the specific gravity, coke value, asphaltum content, water content, ash, flash point, and calorific power. Analyses of three typical asphaltic fuel oils examined by the author are given herewith:—

FUEL OIL FROM CHILE.

Specific gravity - - - .9518 at 20° C.

Retort Test. (Bulb of Thermometer Immersed.)		Engler Flask Distillation.	
13	per cent. at 300° C.	Drop at 185° C.	
24½	„ 350° C.	5	per cent. at 200° C.
32	„ 380° C.	13	„ 250° C.
38	„ 400° C.	20½	„ 280° C.
44	„ 410° C.	23½	„ 300° C.
50	„ 420° C.	32	„ 320° C.
66	„ 430° C.	53	„ 350° C.
77	„ 440° C.	(commences to coke before reaching 380° C.)	

FUEL OIL FROM CHILE—*continued.*

Ignition point in oxygen	-	-	-	264° C.
Gross calorific value	-	10,110 cal.	= 18,198 B.Th.U.	
Net	"	9,476 "	= 17,057 "	
Viscosity (Redwood)	-	387 units at	70° F.	} standard: rape oil = 100 units at 60° F.
"	"	108 "	100° F.	
"	"	15.3 "	200° F.	
Closed flash point (Gray)	-	-	-	114° F.
Asphaltum	-	-	-	11.5 per cent.

Complete Analysis of Oil.

Water	-	-	1.90 per cent.
Carbon	-	-	83.4 "
Hydrogen	-	-	11.5 "
Oxygen and nitrogen	-	-	0.49 "
Sulphur	-	-	2.32 "
Ash	-	-	0.39 "

Complete Analysis Calculated
as Dry Oil Free from Ash.

...
85.37 per cent.
11.77 "
0.50 "
2.36 "
...

VENEZUELAN OIL.

Specific gravity	-	-	-	-	.955 at 20° C.
Ignition point in oxygen	-	-	-	-	275° C.
Gross calorific value	-	9,683 cal.	= 17,429 B.Th.U.		
Net	"	9,083 "	= 16,349 "		
Viscosity (Redwood)	-	934 units at	70° F.	} standard: rape oil = 100 units at 60° F.	
"	"	325 "	100° F.		
"	"	195 "	200° F.		
Closed flash point (Gray)	-	-	-	-	100° F.
Asphaltum	-	-	-	-	13.6 per cent.
Water	-	-	-	-	3.0 "
Sulphur	-	-	-	-	1.68 "
Ash	-	-	-	-	0.24 "
Coke	-	-	-	-	9.8 "

MEXICAN FUEL OIL.

Specific gravity - - - .949 at 20° C.

Retort Test.
(Bulb of Thermometer
Immersed.)

Engler Flask Distillation.

Drop at 312° C.

Drop at 245° C.

2 per cent. at 320° C.

1 per cent. at 250° C.

13½ „ 350° C.

8½ „ 280° C.

23 „ 380° C.

12½ „ 300° C.

31½ „ 400° C.

55 „ 350° C.

43½ „ 420° C.

76 „ 360° C.

(the residue coked at this
temperature.)

Ignition point in oxygen - - - 258° C.

Gross calorific value - 10,350 cal. = 18,630 B.Th.U.

Net „ „ - 9,734 „ = 17,521 „

Viscosity (Redwood) - 267 units at 100° F. { standard : rape
„ „ - 22.2 „ 200° F. { oil = 100 units
at 60° F.

Closed flash point (Gray) - - - 200° F. (froths badly).

Asphaltum - - - 36.8 per cent.

Water - - - 1.0 „

Carbon - - - 83.6 „

Hydrogen - - - 10.9 „

Oxygen and nitrogen - - - 1.48 „

Sulphur - - - 2.85 „

Ash - - - 0.17 „

Coke - - - 12.2 „

Shale Oils.—Shale oils are very similar to petroleum oils, and as they are distillates there is no difficulty caused by asphaltum. They closely resemble petroleum distillates in chemical composition and calorific power, and little difference is noticeable in their behaviour in internal combustion engines. Crude shale oils are seldom used as fuel oils in this country from economical considerations. The quantity of shale oil available in the British Isles is small, the production in 1917 being 230,000 tons, or less than ½ per cent. of the world's production of petroleum.

An examination of a shale oil necessitates the same tests as those employed in valuing crude petroleum.

Lignite Tars and their Distillates.—Lignite tars, obtained by the destructive distillation of lignite, are rich in hydrogen

and very much akin to petroleum and shale oils. Unless they contain quantities of impurities (as water and ash), lignite tars are suitable for Diesel engines. In heat value they are slightly lower than petroleum. The distillates of lignite tars are suitable for use in Diesel and semi-Diesel engines. They are much cleaner than the raw tars, and are slightly higher in specific gravity than the corresponding petroleum fractions. They have been prepared and used in large quantities in Germany, where extensive lignite deposits exist.

Coal Tars and their Distillates.—Coal tars vary very considerably in composition, depending upon the type of coal from which they are obtained, and upon the plant employed for carbonisation. Their respective properties are best judged from the table on p. 96.

The distillates of coal tar are generally suitable for use in Diesel engines, provided that special arrangements are made for their use. Semi-Diesel engines are rarely employed for running on tar oil; therefore in the following remarks the Diesel engine alone will be considered.

The shortage of petroleum became acute on the Continent at a much earlier date than in this country because of high import tariffs. This caused the continental Diesel engine manufacturers to turn their attention to substitute fuels; at first, coal tar creosotes, and later, raw coal tars, being tested. Rieppel,¹ after researches in the laboratory, and engine trials on petroleum, lignite tar distillates, and coal tar distillates, made the following statements:—

1. Lignite tar distillates are suitable for Diesel engines, but coal tar distillates cannot be used without special modifications.

2. For judging the possibility of using an oil, specific gravity, viscosity, flash point, burning point, and calorific power are useless.

3. The hydrogen content of the elementary analysis is of fundamental importance. This value indicates the proportion of aliphatic and aromatic hydrocarbons.

4. The spontaneous ignition and the burning of a fuel depend upon the property which the oil possesses of forming an oil gas, that is, upon the yield of oil gas at relatively low

¹ *Zeits. Ver. d. Ing.*, 1907, p. 613.

pressure and temperature. Coal tar oils require a larger amount of heat or else a longer period of heating than lignite tars.

Zöbell,¹ Allner,² Nägel,³ Aufhäuser,⁴ Graefe,⁵ Russig⁶ and others discussed the properties of fuels in various papers. Constam and Schläpfer⁷ published researches on various fuels, giving a set of analyses which are, to the author's knowledge, the most complete yet published. As a result of these and other investigations the value of the various chemical tests as an indication of the suitability of fuel for Diesel engines is now well understood.

The difficulties encountered in burning liquid coal tar distillates are mainly caused by the comparatively high spontaneous ignition temperatures of these oils. The coal tar products obtained by high temperature carbonisation (as in gas works or coke ovens) consist mainly of aromatic hydrocarbons, whereas the fuels usually employed on Diesel engines, namely petroleum and shale oils, consist mainly of aliphatic and hydro-aromatic hydrocarbons. As fuels the latter bodies are very similar to each other, and are unstable at high temperatures, so that, when heated in an atmosphere of oxygen, they will ignite in the region of 270° C. without the introduction of any flame or spark. The aromatic bodies found in coal tars are not so easily decomposed, and it is found that a temperature of 480° C. is required to cause the spontaneous ignition of these coal tar oils in an oxygen atmosphere. The ignition of the oil in Diesel engines is dependent on the heat caused by compression, no special ignition device being provided. The temperature attained in the cylinder under ordinary circumstances is sufficient to cause ignition when petroleum oil is used, but fails to regularly ignite tar oils. An evident remedy for this trouble is to increase the compression of the engine until the necessary cylinder temperature is attained.

It is found in practice that the normal Diesel engine

¹ Zöbell, "Petroleum," vol. iv, p. 946; "Der Oelmotor," vol. i., p. 31.

² Allner, *Journ. f. Gasbeleuchtung*, 1911, p. 1025.

³ Nägel, *Zeits. Ver. d. Ing.*, 1911, p. 1319.

⁴ Aufhäuser, paper before Schiffbautechnischen Gesellschaft.

⁵ Graefe, "Der Oelmotor," 1913, vol. ii., p. 449.

⁶ Russig, "Petroleum," vol. iii., p. 900.

⁷ Constam and Schläpfer, *Zeits. Ver. d. Ing.*, 1913, p. 1489.

compression of 450 to 500 lbs. per square inch has to be raised to about 560 or 580 lbs. per square inch to attain satisfactory results at moderate loads, while lower loads require higher pressure. This necessitates a specially heavy design of engine, and it is not desirable to increase the working pressures of Diesel engines, as they are already higher than other engine pressures.

We may briefly enumerate the more important methods

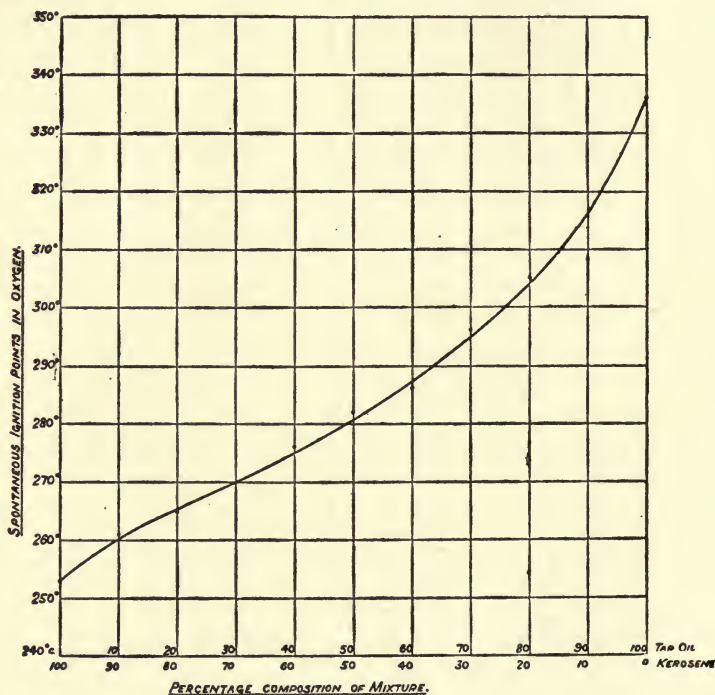


FIG. 9.—Ignition Points of Mixtures of Tar Oil and Kerosene.

of burning tar oils in Diesel engines under the following headings:—

1. To heat the oil, the injection air and the suction air.
2. To mix tar oil with petroleum oils.
3. To increase the compression ratio.
4. To employ an ignition oil.
5. To inject a small tar oil charge prior to the main tar oil charge.

The first method aids combustion, but will not overcome difficulty of starting unless a special oil is employed for this purpose. At low loads irregular running may be encountered.

The mixing of fuels was experimentally investigated by Rieppel,¹ who tested mixtures containing from 10 to 90 per cent. of gas oil. He found that in order to obtain good running, 75 per cent. of the petroleum oil was required,

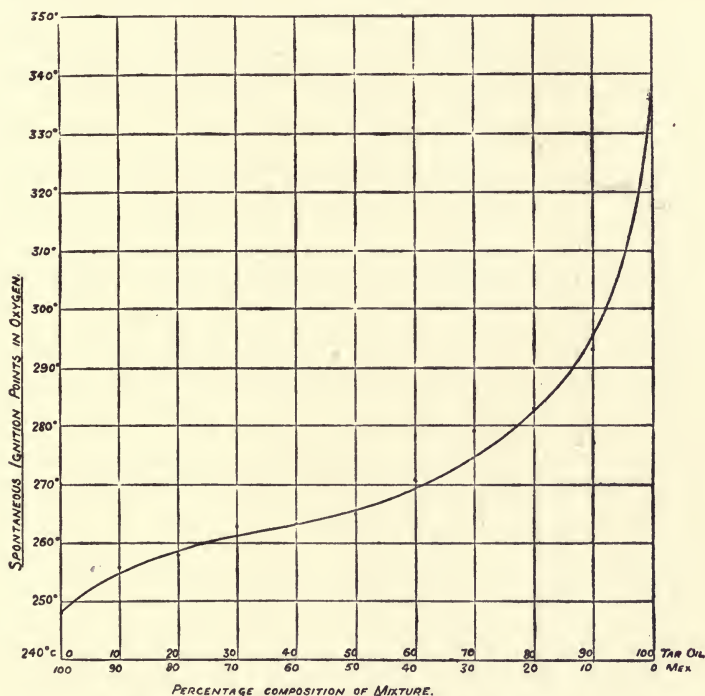


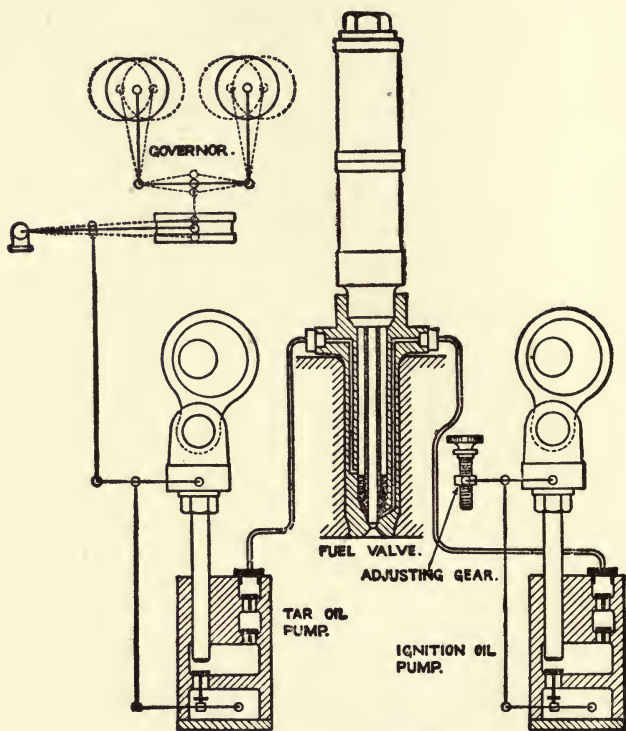
FIG. 10.—Ignition Points of Mixtures of Tar Oil and Petroleum Residuum.

which makes this scheme of no economic advantage, as the petroleum oil must be of good quality to allow mixing with tar oil. The author finds that by adding many kinds of petroleum residuum to tar oil a tarry sticky precipitate is deposited, which completely excludes such mixtures from use.

The author has made experiments on the spontaneous

¹ Rieppel, *Zeits. Ver. d. Ing.*, vol. 51, No. 16, 20th April 1907.

ignition temperatures of mixtures of petroleum and tar products in varying proportions, the results of which are shown in the two accompanying curves, Figs. 9 and 10. The possibility of utilising such mixtures without the aid of ignition oils is dependent upon their spontaneous ignition temperatures.



**DIAGRAMMATIC ARRANGEMENT OF
FUEL PUMPS FOR TAR OIL ENGINE.**

FIG. 11.

Increasing the compression ratio is a simple matter (by introducing more compression plates between the big end bearing and the connecting rod), but although this may be done with existing engines, it is very undesirable to subject engines to pressures beyond those for which they are designed. The higher temperatures obtained with increased compression

must be considered, and a larger compressor is also required. Starting and running on low loads are not satisfactory, even when the compression is raised to 580 lbs. per square inch.

The use of ignition oil is the most satisfactory method at present in use. The engine is provided with an extra fuel pump. Tar oil is introduced into the cylinder in the usual manner, but the extra fuel pump delivers a smaller charge of some easily inflammable oil (any shale oil, or a good quality petroleum oil). The ignition oil is led to the atomiser in such a way as to lie between the fuel valve seat and the main charge of tar oil. Thus, when the fuel valve opens, a small separate charge of the more easily inflammable oil first enters

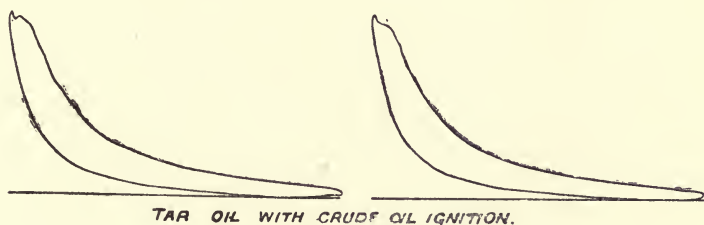


FIG. 12.

the cylinder (before inner dead centre) and heats the combustion space to a sufficiently high temperature to cause immediate and regular ignition of the tar oil. The ignition pump does not require to be under the control of the governor, as the quantity of ignition oil required is the same for all loads. This method yields excellent running at all loads. The proportion of ignition oil required is approximately 6 per cent. at full load. The accompanying diagram¹ (Fig. 11) shows clearly the arrangement of the fuel pumps on an engine fitted for burning tar oil on the pilot ignition system. The indicator cards obtained when an engine is running on the pilot ignition system generally show a distinct mark where the ignition oil ceases and the tar oil commences to burn. Two typical indicator diagrams obtained by the use of pilot ignition are shown in Fig. 12.

The use of specially designed fuel valves, which allow a

¹ C. Day, paper read before the Diesel Engine Users' Association, 19th January 1916.

small portion of the tar oil to enter the cylinder prior to a main charge of the same fuel, have met with some success on larger engines. The introduction of a small quantity of the tar oil in advance of the full charge causes the ignition to be more regular, but, in the author's experience, the tar oil pilot charge is not nearly so satisfactory as a petroleum oil used with special fuel pump.

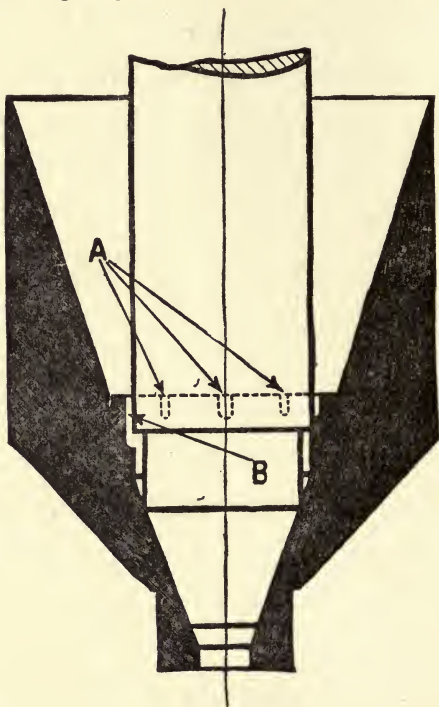


FIG. 12A.

The accompanying drawing (Fig. 12A) shows a device made by the author.¹ It is a ported bottom fuel casing, the piece fitting into the standard bottom fuel valve casing and forming a seat for the fuel valve.

The lower end of the fuel valve is turned so as to have a shoulder which closes the ports marked A, until the valve has been raised a short distance. One port is made specially

¹ Moore, "Tar Oil on Diesel Engines," paper read before Diesel Engine Users' Association, 26th May 1918.

deep to reach below the shoulder, and provide a passage to the fuel valve face when the fuel valve is closed. When the needle valve is on seat there is no way through to the combustion space, but on being slightly raised there is a very restricted way through the single port B. On raising the fuel valve further the several ports A are opened simultaneously, and the main charge of tar oil is introduced. The fuel cam is set to give the opening of the ports A about inner dead centre, when B should commence to operate some 15° before inner dead centre when the valve first opens. Thus a small charge of tar oil is introduced into the cylinder prior to the main tar oil charge. This device certainly had the effect of improving ignition.

Drexler¹ has suggested the use of catalytic agents as a means of aiding the ignition and burning of tar oils, but this method has not been used in practice. The principle is a matter of common usage in many chemical reactions. A catalytic agent is a substance which promotes a chemical reaction, but itself remains in the same state at the end of the reaction as at the commencement. By the introduction of a catalyst, it is possible to obtain many chemical reactions which would otherwise present extreme difficulty. The introduction of a suitable catalytic agent into the cylinder of an internal combustion engine might prove of immense benefit, but there are many difficulties to be overcome before such a device could meet with success on a practical scale. The "tar oil" employed on Diesel engines is generally the creosote, the anthracene oil, or a mixture of both these fractions obtained by the tar distiller. Naphthalene and anthracene may be extracted, but frequently all solid hydrocarbons are left in the oil, any difficulty from obstruction of pipes being overcome by warming the fuel tanks.

Tar oil is used on a large scale on the Continent, and the German Tar Distillers' Federation have adopted the following specification² to guarantee satisfactory quality in tar oils for Diesel engines:—

1. The tar oil must not contain more than 0.2 per cent. solid constituents insoluble in xylol. The incom-bustible matter must not exceed 0.05 per cent.

¹ Reprint from "Der Oelmotor," 1913. Verlag für Fachliteratur, Berlin.

² Rath u. Rossenbeck, Glückauf, 13th May 1911.

2. The water shall not exceed 1 per cent.
3. The coking residue must not be greater than 3 per cent.
4. By distillation at least 60 per cent. by volume must be over at 300° C.
5. The net calorific value shall not be less than 8,800 calories.
6. The flash point must not be lower than 65° C.
7. The oil must be quite liquid at 15° C. On cooling to 8° C., and allowing to rest at this temperature for a period of half an hour, no precipitation must take place.

This specification is somewhat unnecessarily rigid, and if used in this country would certainly tend to raise prices. The following specification has therefore been suggested for use in this country :—¹

1. The tar oil must be a product of the distillation of coal tar. No product must be present which has not undergone distillation.
2. Tar oil must not contain more than 2 per cent. of solid constituents insoluble in xylol.
3. The ash content must not be greater than 0.08 per cent.
4. The water content should not be greater than 2.5 per cent.
5. The coking residue must not exceed 3 per cent.
6. The oil must be liquid at 60° F., when maintained at that temperature for half an hour.
7. In case of crystals settling in the transport tank, the buyer to be allowed to drain off the liquid portion and to return the solid to the sender.

Note.—Clauses 6 and 7 might be omitted, as their inclusion in the specification will tend to raise the price. They can safely be omitted if means are taken to warm the oil before using.

The oxygen-containing bodies present in tar oils are generally acidic, and can be extracted by washing with caustic soda. These substances are known as "tar acids," and consist mainly of phenol and the three isomeric cresols (ortho, meta, and para cresols). These compounds do not in any way injure the working parts of an engine, but make it advisable to dispense with copper service pipes.² They burn quite satisfactorily. They are, however, lower in calorific power than the hydrocarbon portion of an oil, and

¹ C. Day, paper read before Diesel Engine Users' Association, 19th January 1916.

² Deposits found in the pulveriser casings of Diesel engines, which have been running on tar oils, have been proved by analysis to contain large quantities of copper, evidently originating from the fuel service pipes.

tend to lower the calorific value of a fuel. In investigating this point the author examined a tar oil and obtained the following figures of the gross calorific values of the oil before and after washing, and also of the tar acids:—

Tar oil containing 13 per cent. of tar acids	-	yielded	9,253 cal.
The same after removal of tar acids	-	„	9,501 „
The tar acids alone	-	„	7,995 „

Providing that the tar oil is the creosote of a horizontal retort tar, and is not excessively rich in naphthalene, the author found that the heat value could be roughly ascertained from the tar acid content by the following rule:—

$$\text{Gross calorific value} = 9,900 - 50 T \text{ cal.},$$

where T is the percentage of tar acids.

Tar oils from the same type of tar do not vary much in calorific power, except such variation as is due to the tar acid content.

A few typical analyses of tar oils which have recently been examined by the author are given herewith:—

HORIZONTAL RETORT TAR OIL.

Specific gravity - - - 1.049 at 20° C.

Retort Test.

(Bulb of Thermometer Immersed.)

Drop at 190° C.

28 per cent. at 250° C.

67 „ 300° C.

Gross calorific value	-	9,191 cal.	= 16,544 B.Th.U.	
Net „ „	-	8,813 „	= 15,863 „	
Viscosity (Redwood)	-	10.3 units at 70° F.	} standard: rape oil = 100 units at 60° F.	
„ „	-	8.5 „ 100° F.		
„ „	-	6.0 „ 200° F.		
Closed flash point (Gray)	-	-	-	200° F.
Asphaltum	-	-	-	None.
Tar acids	-	-	-	14 per cent.
Water	-	-	-	0.60 „
Carbon	-	-	-	89.7 „
Hydrogen	-	-	-	7.4 „
Oxygen and nitrogen	-	-	-	2.25 „
Sulphur	-	-	-	0.65 „
Ash	-	-	-	Traces.
Coke	-	-	-	None.
Mechanical impurities	-	-	-	None.

LIQUID FUELS

VERTICAL RETORT TAR OIL.

Specific gravity - - - 1.016 at 20° C.

Retort Test.
(Bulb of Thermometer
Immersed.)

Engler Flask Distillation.

Drop at 155° C.
27 per cent. at 250° C.
67 " 300° C.

Drop at 120° C.
3 per cent. at 200° C.
46 " 250° C.
76 " 300° C.
(Sp. gr. of distillate, .996.)

Gross calorific value	-	9,189 cal.	=	16,540 B.Th.U.	
Net " "	-	8,762 "	=	15,772 "	
Viscosity (Redwood)	-	9.7 units at 70° F.	} standard: rape oil = 100 units at 60° F.		
" "	-	7.0 " 100° F.			
" "	-	5.6 " 200° F.			
Closed flash point (Gray)	-	-	-	190° F.	
Asphaltum	-	-	-	None.	
Tar acids	-	-	-	28 per cent.	
Water	-	-	-	0.70 "	
Carbon	-	-	-	85.75 "	
Hydrogen	-	-	-	7.92 "	
Oxygen and nitrogen	-	-	-	5.14 "	
Sulphur	-	-	-	0.49 "	
Ash	-	-	-	Traces.	
Coke	-	-	-	None.	
Mechanical impurities	-	-	-	None.	

BLAST FURNACE TAR OIL.

Specific gravity - - - .903 at 20° C.

Retort Test.
(Bulb of Thermometer
Immersed.)

Engler Flask Distillation.

Drop at 201° C.
94 per cent. at 250° C.

Drop at 185° C.
20 per cent. at 200° C.
82 " 225° C.

BLAST FURNACE TAR OIL—*continued*.

Gross calorific value	-	9,992 cal.	= 17,986 B.Th.U.	
Net	„ „	9,603 „	= 17,286 „	
Viscosity (Redwood)	-	5.7 units at 70° F.	{ standard: rape oil = 100 units at 60° F.	
Closed flash point (Gray)	-	-	-	158° F.
Asphaltum	-	-	-	None.
Tar acids	-	-	-	23 per cent.
Water	-	-	-	None.
Carbon	-	-	-	82.6 per cent.
Hydrogen	-	-	-	9.9 „
Oxygen and nitrogen	-	-	-	7.22 „
Sulphur	-	-	-	0.28 „
Ash	-	-	-	None.
Coke	-	-	-	None.
Mechanical impurities	-	-	-	None.

Results of a very large number of analyses of both tar oils and petroleum oils used in this country are given in the accompanying table¹ (see p. 90).

Naphthalene.—Solid naphthalene, in the crude state, has been successfully employed as a fuel for Diesel engines, and in Germany a considerable amount of naphthalene finds use as fuel. Special engines are designed for this fuel, in which the naphthalene is passed into jackets situated near the cylinder head, and so arranged as to be heated by the circulating water, whereby it is melted before entering the fuel pump.

Bruhn² gives the following figures for the output of naphthalene engines in Germany:—

Year.	Number of Engines Made.	Aggregate H.P.	Metric Tons of Naphthalene Consumed.
1911 - - -	68	678	75
1912 - - -	283	2,961	509
1913 - - -	367	3,934	1,423

¹ Moore, "Tar Oil on Diesel Engines." Paper read before Diesel Engine Users' Association, 26th May 1918.

² H. K. Bruhn, *Journ. f. Gasbeleuchtung*, 2nd and 9th November 1915.

LIQUID FUELS

Property.	Coal Tar Distillates.			Petroleum Oils.		
	Average.	Maximum.	Minimum.	Average.	Maximum.	Minimum.
Specific gravity	1.017	1.090	.950	.906	.960	.858
Water per cent.	1.08	12.0	None	0.91	9.5	None
Carbon per cent.	89.2	90.0	87.1	85.39	88.32	83.4
Hydrogen per cent.	7.3	8.0	6.5	11.51	12.5	10.9
Oxygen and nitrogen per cent.	3.9	4.8	3.0	1.28	2.2	0.072
Sulphur per cent.	0.636	1.02	0.28	1.27	2.85	0.042
Ash per cent.	0.005	0.10	None	0.045	0.39	None
Closed flash point ° F.	164.	208	97	187	280	Below 60
Viscosity in units Redwood at 70° F.	8.6	23	6.8	777	4800	9.4
Heat value { Gross B.Th.U.	17,365	17,946	16,400	19,000	19,656	17,606
Engler distillation per cent. at 250° C.	16,597	17,174	15,903	17,809	18,459	16,526
Retort test per cent. at 350° C.	58	76	28	5	13	1
Coke yield per cent.	79½	94	51	19	24	12½
Free carbon per cent.	28.5	30	13½
Tar acids per cent.	3.3	14.7	1.3	2.83	12.2	0.24
Asphaltum per cent.	0.26	5.2	None
Temperature of spontaneous ignition ° C.	9.5	30.0	Traces

	480	520	415	12.0	36.8	1.54
				264	264	254

Only Gasworks and Coke Oven Tar Distillates and "Diesel Engine Tar Oils" included.

Heavy distillates from coke oven tars are very similar to the creosotes obtained from gas works tars, and require similar treatment when burned in Diesel engines. The oils obtained by the distillation of blast furnace tars and producer-gas tars are generally suitable for use in Diesel engines when an ignition oil is employed.

Raw Coal Tars.—Burning raw coal tars in Diesel engines presents further difficulties in addition to those encountered in the use of the tar oils.

The difficulties of ignition may be overcome by the methods already enumerated for tar oils, but additional difficulties are encountered on account of the tars generally containing free carbon, frequently accompanied by water and ash. The free carbon is the most serious consideration with raw tars. Small percentages of free carbon may be burned without difficulty, but when over 10 per cent. of this substance is present the exhaust valve becomes very badly pitted, and the exhaust temperature is high, and there is often a smoky exhaust. This action is due to the slow burning of the particles of free carbon, which, when not completely consumed during the working stroke, pass from the engine in a glowing state. This can be proved by opening the indicator cock of the engine, when it will be noticed that the number of sparks bear a direct relationship to the free carbon content of the fuel. These glowing particles of carbon become trapped under the exhaust valve face and produce an appearance similar to beaten metal-work. The free carbon does not consist of pure carbon, but is best considered as coke in an exceedingly finely divided state (see p. 123). The removal of free carbon is very difficult, though Müller¹ was able to extract two-thirds of the free carbon from water-gas tar by centrifugal treatment. The removal of free carbon by filtration presents many difficulties, mainly on account of the large quantities of this body which have to be handled. The commercial extraction of free carbon from horizontal retort tars by filtration is not very promising, as even if the removal could be completely and economically effected the reduction in the quantity of tar is a serious consideration. In practice it is

¹ Müller, "Ueber Entwässerung des Wassergasteers," *Journ. f. Gasbel-cuchtung*, 1912, p. 229.

impossible to prevent the loss by tar being removed together with the free carbon. To make this process successful with tars containing 25 to 30 per cent. of free carbon it would be necessary to find a market for this by-product. Hitherto it has been usual among Diesel engine users only to employ such tars as contain a sufficiently low percentage of free carbon to allow of them being burned without any treatment. The tars obtained from vertical retorts are generally low in free carbon content, and have been employed on a large scale in Germany, where the Dessau vertical retorts are largely used for gas manufacture. Vertical retort tars also contain large quantities of aliphatic hydrocarbons, which to some extent aid their ignition and combustion. Fig. 13



VERTICAL RETORT TAR WITH KEROSENE IGNITION.

FIG. 13.

shows two indicator diagrams taken from a 50 B.H.P. Mirrlees-Diesel engine, when running on vertical retort tar with kerosene as ignition oil.

Dr. Diesel estimated that the tar produced in Germany would, if used in Diesel engines, yield sufficient power for all the industrial purposes of that country, and leave sufficient for their entire navy. The tars of this country¹ are generally higher in free carbon content than those produced on the Continent, as the majority of British gas works employ horizontal or inclined retorts, which yield heavy viscous tars containing 15 to 30 per cent. of free carbon. The high viscosity of these products is also an undesirable feature. The newer installations in this country are, however, mainly vertical retort plants. Some of the coke oven tars can be used in Diesel engines, but different types of coke oven yield

¹ H. Moore, paper read before the Manchester Association of Engineers, "Fuel Oils from Coal," 26th February 1916.

tars of widely varying properties. The author has run a 50 B.H.P. Mirrlees-Diesel engine in trials extending over six months on raw tar from Simon-Carvé coke ovens. A typical indicator card taken during this trial is shown in Fig. 14. The tar produced from carburetted water-gas plants, although a product of gas works, is not a coal tar, but is the residue left after cracking petroleum or shale-gas oils. It is therefore different in composition from other tars. It is known as carburetted water-gas tar, or as oil-gas tar. It is mainly composed of aromatic hydrocarbons, but contains a sufficient quantity of other hydrocarbons to give it a comparatively high hydrogen content (about 7 per cent.).

Oil-gas tar is not available in sufficient quantity to make

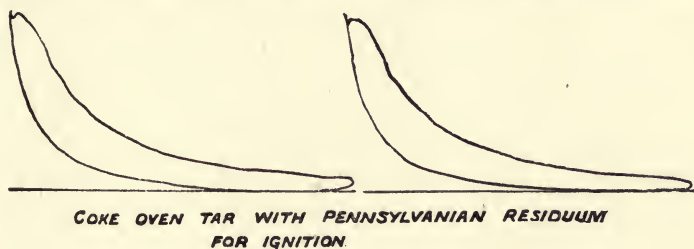


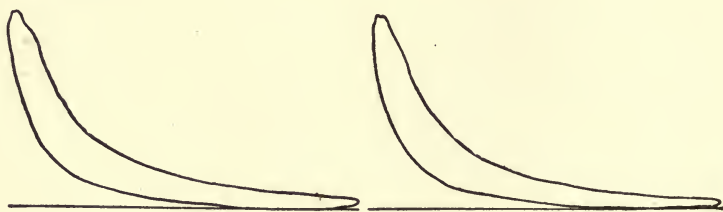
FIG. 14.

it an important fuel, and is frequently mixed with water (in the form of emulsions) in such quantity as to make it useless as fuel until the water is removed. The most successful method of separating the water is by centrifugal treatment of the warmed mixture.¹ Other methods (settling, or adding salt and settling) can be employed with some tars, but are not always successful. Two indicator cards taken by the author from a 50 B.H.P. Mirrlees-Diesel engine when running on oil-gas tar and on a residue of oil-gas tar respectively are shown in Figs. 15 and 16, kerosene being used as ignition oil in both cases. The properties of several British tars can be seen in the table on p. 96.

Ash content seriously interferes with the use of tars as fuels, and no successful process has yet been found for the entire removal of this substance without resorting to distilla-

¹ *Journ. of Gas Lighting*, 1915, 130, p. 196.

tion. Tars with more than 0.08 per cent. of ash are generally unsuitable for internal combustion. Producer-gas tar is generally unsuitable for use in internal combustion engines in the raw state on account of the high proportion of water and ash. Blast furnace tars generally contain ash in large quantities, and are therefore not suitable for engine use in the raw state.



OIL GAS TAR WITH KEROSENE IGNITION.

FIG. 15.

The use of raw coal tars in this country is certain to increase in the near future on account of the low price of these fuels (usually about one-third the price of creosote): they also, together with the tar oils, have the advantage of being produced at home. As the yield of tar oil (creosote and anthracene oils) from tar is seldom over 35 per cent., a much



OIL GAS TAR RESIDUUM WITH KEROSENE IGNITION.

FIG. 16.

larger amount of fuel is available when the raw tar is employed. The distilled products generally sell at a little over twice the price of the raw tar, while they are but slightly superior in calorific power. Tar oils produce about 12 per cent. less power per unit weight than average petroleum fuel oils.

The production of tars in this country is difficult to estimate

as no official figures are available. Gray and Mellanby¹ estimated the production of coal tars in Great Britain for 1911 at:—

Coal-gas tar	-	-	-	785,000 tons,
Coke oven tar	-	-	-	300,000 „
Blast furnace tar	-	-	-	145,000 „
Producer tar	-	-	-	25,000 „

and the production of carburetted water-gas tar for the same year at 70,000 tons.

Analyses of several varieties of British tars and tar oils, together with an analysis of a typical petroleum oil, are shown in the accompanying table (p. 96).²

Wood Tars.—The tars obtained by the destructive distillation of wood have not to the author's knowledge been used as oil engine fuels on account of their being of greater value for other industrial purposes, and there is no likelihood of their entry into the fuel market in the future.

Peat Tars.—Peat tars would probably be suitable for fuel, but though there is an abundance of peat within the British Isles the difficulties of economic distillation have hitherto prevented the preparation of sufficient oil to allow of its entry into the fuel market. They may, however, become of importance in the near future, as experiments are being made on a large scale at present.

Animal and Vegetable Oils.—These are generally not produced in sufficient quantities, or at a sufficiently low price, to allow of their entry into the fuel oil market, where low cost and large quantities are essential, except for use under abnormal circumstances. The author has run a Diesel engine on whale oil with complete success, the consumption of this product per brake horse power being very moderate. The combustion was excellent, and no injurious effect was noticeable on the engine. An indicator diagram taken while running on the fuel showed normal combustion. The engine

¹ Gray and Mellanby, paper read before the Inst. of Engineers and Shipbuilders in Scotland, 1914.

² H. Moore, paper read before the Manchester Association of Engineers, 26th February 1916.

ANALYSES OF FUEL OILS.

Description.	Sp. Gr. at 15° C.	Water.	Ultimate Composition.				Ash.	Coke.	Net Calorific Value.		Free Carbon.
			C.	H.	O. & N.	S.			Calories.	B.Th. U.	
Horizontal retort tar - - -	1.180	1.75	91.5	5.2	2.6	0.5	0.20	24.0	8,645	15,561	18.2
Inclined retort tar - - -	1.157	1.11	89.9	6.0	3.6	0.5	0.02	18.5	8,671	15,626	14.0
Vertical retort tar - - -	1.089	2.25	88.0	6.8	3.8	0.6	0.03	6.1	8,664	15,613	1.7
Otto Hilgenstock coke oven tar -	1.208	6.00	90.0	5.4	3.8	0.8	0.02	26.8	8,624	15,523	23.9
Simon-Carvé coke oven tar - -	1.090	0.50	88.1	5.6	6.1	0.2	0.07	6.0	9,261	16,670	Traces
Chamber oven tar - - -	1.082	1.29	88.2	6.9	4.6	0.3	Traces	7.3	8,737	15,727	3.0
Low temperature carbonisation tar -	1.058	3.00	85.8	8.1	5.49	0.09	0.11	8.2	8,776	15,797	2.2
Water-gas tar - - -	1.054	0.59	92.2	6.8	0.4	0.6	Traces	18.7	8,647	15,563	6.8
Blast furnace tar - - -	1.172	3.0	89.5	5.75	0.55	0.84	0.36	23.4	8,288	14,918	9.5
Blast furnace tar oil - - -	0.974	None	87.25	9.8	2.59	0.36	None	1.05	9,243	16,637	None
Oil distilled from low temperature tar	0.884	"	85.6	11.4	2.48	0.4	"	0.84	9,558	17,204	"
Horizontal retort tar oil - - -	1.065	1.00	90.1	6.8	2.4	0.50	0.2	3.0	9,243	16,637	"
Pennsylvanian petroleum fuel oil -	0.889	None	86.7	12.55	0.11	0.64	Traces	0.60	10,108	18,194	"

was not specially prepared, the adjustments being in normal position as used for petroleum oils. No ignition oil was required.

The whale oil on analysis yielded the following figures :—

Specific gravity	-	-	-	·921 at 20° C.
Gross calorific power	-	-	-	9,342 cal. = 16,815 B.Th.U.
Viscosity	-	25·8 Redwood units at 100° F. (partly solid at 70° F.).		
Closed flash point (Gray)	-	-	-	over 320° C.
Sulphur	-	-	-	0·13 per cent.
Ash	-	-	-	traces only.
Coke value	-	-	-	1·27 per cent.
Water	-	-	-	traces only.

It appears probable from analyses that all animal oils would be satisfactory for use in Diesel engines, though on account of their deficiency in calorific power the fuel consumption in all cases would be higher than with petroleum.

Vegetable oils from a fuel standpoint are very similar to animal oils; they contain oxygen, and therefore are lower in heat value than the petroleum oils. They are rarely used as fuels on account of their being able to command higher prices for other industrial purposes.

Dr. Rudolph Diesel suggested the use of arachis oil (peanut oil) as a motive fuel for Diesel engines, and found by engine trials that the consumption of this fuel was about 16 per cent. greater than that of a petroleum fuel oil of 10,000 net calorific power. Constam and Schläpfer found the net calorific power of arachis oil to be 8,866 cal., and the elementary composition to be :—

Carbon	-	-	-	-	77·3 per cent.
Hydrogen	-	-	-	-	11·8 „
Oxygen and nitrogen	-	-	-	-	10·8 „
Sulphur	-	-	-	-	0·1 „

Palm oil has a specific gravity of about ·915, and a net calorific power of 8,800 cal.

There is little likelihood of vegetable oils becoming of importance as fuels except in isolated stations far removed from supplies of ordinary fuels, and where there is an abundance of vegetable oil.

Methyl and ethyl alcohols are generally too expensive to allow of their use in heavy oil engines ; besides, they can be economically burned in an alcohol engine, which has a much lower initial cost than the corresponding size of Diesel or semi-Diesel engine. Ethyl alcohol can be used with efficiency on a Diesel engine, but, on account of its high ignition temperature, it is necessary to employ an ignition oil to obtain regular firing. The author found that it was in no way deleterious to the engine, and yielded a higher thermal efficiency than any other fuel he had tested, the high thermal efficiency being probably the result of the low viscosity of the fuel.

PART III

CHAPTER XI

THE EXAMINATION OF LIQUID FUELS

Sampling.—The importance of obtaining a sample representative of the bulk of the liquid cannot be exaggerated. The author's experience has been that errors in sampling are much more frequent than analytical mistakes.

In sampling deliveries from wagons either a small continuous stream of liquid may be by-passed into a sample tin when the tank is being emptied, or small amounts may be withdrawn from the stream flowing from the tank wagon at equal intervals, and mixed to form the larger sample.

For most purposes a quart sample is sufficient. When deliveries are in drums or barrels, a satisfactory method of sampling is by *slowly* inserting a glass tube through the bung hole. When the tube reaches the base of the drum the thumb is pressed over the upper end of the tube, and the tube, including the sample liquid, is withdrawn. This procedure is repeated until the necessary amount of sample is obtained. The tube for this purpose should be of glass, about $\frac{1}{2}$ in. bore, and should not be much longer than the depth of the drum. By closing the upper end during the insertion of the tube, and opening while the tube is at the bottom of the oil, it is possible to withdraw a sample of any water or sand which lies at the bottom. With tars and tar oils of high gravity the water is either mixed throughout the mass, or collects in a layer at the top of the fuel. When sampling large tanks an iron pipe may be used with advantage. The bottom end of the pipe can be best closed by means of a conical plug attached to a wire passing through the inside of the tube.

Glass, earthenware, or tinned iron vessels may be used to

contain samples. Iron surfaces react with the sulphur in the oil. Stoppers should be very secure and not porous.

When samples have to travel long distances a tin vessel with stopper soldered fast is most suitable. Samples should not be left exposed to air, as they then lose their volatile products. The sampler should in all cases be observant, and note any sediment or crystals, and should exercise intelligence in attaining a perfectly representative sample.

The Examination of the Physical and Chemical Properties of Liquid Fuels.—A great variety of tests may be made on liquid fuels, and though generally only a few of these are required, under special circumstances any one of them may be of fundamental importance. The value and meaning of the results of each test will be given together with the analytical procedure, and the author hopes thereby to assist the engineer in deciding, firstly, to which tests an oil must be subjected; and, secondly, the behaviour which is to be expected from a fuel of any given analysis.

The following is a list of the more important tests to which liquid fuels may be subjected:—

Calorific power.	Combustion.
Specific gravity.	Sulphur content.
Flash point.	Naphthalene content.
Burning point.	Anthracene content.
Viscosity.	Tar acids content.
Cold test.	Tar bases content.
Coke test.	Temperature of spontaneous
Water content.	ignition.
Asphaltum content.	Specific heat.
Mechanical impurities.	Vapour pressure.
Free carbon.	Vapour density.
Ash.	Latent heat of vaporisation.
Fractional distillation.	Iodine value.

These tests do not all apply to the same class of fuels; for example, it would be useless to test kerosene for free carbon, which is not found in distillates. Several of these tests apply to one type of fuel only.

The calorific value will be treated apart on account of its

THE EXAMINATION OF LIQUID FUELS 101

importance and the length of description necessary to deal adequately with the subject.

Specific Gravity.—The specific gravity is the weight of a volume of the fuel relative to the weight of an equal volume of water at 15° C. For purely scientific purposes it is usual to take water at 4° C. (the point of maximum density) as unity, but for most industrial purposes a temperature of 15° C. is used as a standard. Of the many methods available only the more important ones need be mentioned. These are by means of the specific gravity bottle, the pyknometer, the hydrometer, and the Mohr-Westphal specific gravity balance.

The usual form of specific gravity bottle (Fig. 17) is a small vessel of glass fitted with a glass stopper. The stopper is pierced with a fine hole. The bottle is of some definite capacity, and is filled to the top with the liquid under examination, care being taken to exclude air bubbles. On replacing the stopper any excess of liquid will escape through the capillary, when the bottle may be wiped clean on the outside and weighed. The weight of fuel is then obtained by subtracting the weight of the



SPECIFIC GRAVITY BOTTLE.

FIG. 17.

empty bottle from the weight of the bottle and oil together. On dividing by the capacity of the bottle the specific gravity is obtained. It is always advisable to standardise these bottles with water at 15° C., in order to ensure that the capacity be correctly stated. In case of the capacity not being correct it is necessary to make allowance in the calculation.

All specific gravity readings should be taken in the region of the temperature at which they are to be stated (generally 15° C.). A correction for a slight difference in temperature may be made by allowing for the coefficient of expansion of the oil. For hydrocarbon fuel oils this is generally about $\cdot 00072$ per

degree Centigrade, or $\cdot 0004$ per degree Fahrenheit ; the specific gravity falling with increase in the temperature of the oil.

Pyknometers (Fig. 18) are tubes of various designs which are drawn into capillaries at each end. The liquid under test is drawn into the apparatus by means of a pump, and the levels adjusted to certain points. The calculation is the same as in the case of the specific gravity bottle.

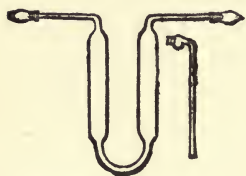


FIG. 18.—Pyknometer.

The hydrometer (Fig. 19) is a float provided with a narrow stem and so balanced that the stem only projects from the liquid under examination. As the weight of liquid displaced by a floating body is equal to the weight of the body, it is evident that the depth of the float immersed will increase with light liquids, and decrease with heavy liquids. By graduating the narrow stem it is possible to read the gravity directly. Hydrometers are usually made of glass and weighted at the base with mercury or leaden shot. By using sets of hydrometers reading over different ranges of gravity, as, for example, $\cdot 800$ to $\cdot 850$; $\cdot 850$ to $\cdot 900$; $\cdot 900$ to $\cdot 950$, etc., it is possible to obtain very delicate readings in this way. Although not so accurate as the previously mentioned method, the hydrometer is the most generally used method of determining the density of liquids on account of the rapidity and simplicity of the operation. For technical purposes specific gravities of fuel oils are not required to be more accurate than the third decimal place, a degree of accuracy readily obtained with the hydrometer.

In addition to the ordinary scale of readings based on the density of water there are in common use the Twaddell scale, used occasionally among tar distillers, and the Baumé scale, used largely in the American petroleum industry. Also there is another Baumé scale in this country, which, however, is seldom used in connection with liquid fuels.

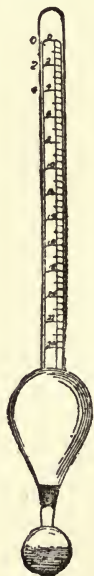


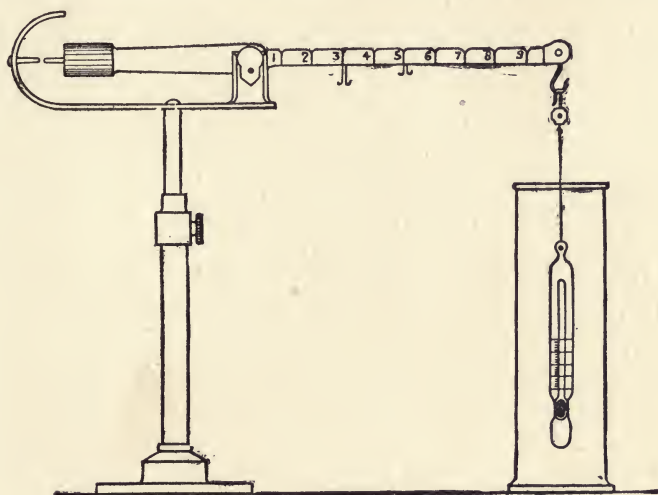
FIG. 19.
Hydrometer.

To convert degrees Twaddell to specific gravity for liquids heavier than water, multiply the degrees Twaddell by 5 ; add 1,000, and divide result by 1,000, thus :—

$$12^{\circ} \text{ Tw.} = \frac{(12 \times 5) + 1000}{1000} = 1.06 \text{ specific gravity.}$$

For the conversion of American Baumé degrees to specific gravity, and vice versa, consult the table on p. 196.

The Westphal specific gravity balance (Fig. 20) is an instrument working on the same principle as the hydrometer.



WESTPHAL SPECIFIC GRAVITY BALANCE.

FIG. 20.

The arm holding the plummet is divided into ten equal parts by nine notches. The balance is so made that when the plummet is in air the pointers are opposite without the addition of any riders. The largest rider is of such a weight that when it is suspended from the plummet hook and the plummet immersed in water at 15° C. the balance is again in equilibrium. Smaller riders of $\frac{1}{10}$, $\frac{1}{100}$, and $\frac{1}{1000}$ the weight of the first rider are provided.

The method of operation is to immerse the plummet in the liquid under examination, and then to place riders in the notches in the plummet arm until equilibrium is obtained.

The heaviest rider is added first, as when placing weights on a balance or on a pair of scales. The specific gravity is then read from the position of the riders, in order of their size. For example, if the largest rider be at notch 8, the second rider at notch 5, the third at notch 6, and the smallest rider at notch 3, the reading would be .8563.

A thermometer for indicating the temperature of the liquid is situated in the plummet. Viscous liquids naturally interfere with the operation of this instrument.

The specific gravity as a means of valuation of liquid fuels is of great importance. It generally shows whether the fuel be of petroleum or coal tar origin, as the latter range of products have much higher gravities than the former. Taken in conjunction with the boiling point of a fraction, it enables one roughly to estimate the proportion of aromatic compounds in a hydrocarbon oil of mixed composition. The specific gravity in the case of a sample of depetrolised crude petroleum generally indicates whether the oil be of asphaltic or paraffin base (a very important matter in connection with heavy oil engines).

It gives an approximation of the boiling point if the type of product be taken into consideration. In this respect it may in some cases be misleading, as when comparing hydro-aromatic oils with aliphatic oils, if allowance be not made for this fundamental difference.

By comparison of the specific gravity of the oil with that of other oils of similar origin it is possible to get a rough idea of what is to be expected with regard to its other properties. For rough generalisations the following figures are of assistance :—

Petroleum.			Specific Gravity.
Distillates	Petrols	-	.690-.750
	Kerosene	-	.800
	Gas oils	-	.840-.870
Crude petroleum -			.800-.950
Depetrolised petroleum			.870-.950
Tars and Products.			Specific Gravity.
Horizontal retort tars			1.10-1.20
Vertical retort tars			1.00-1.10
Distillates	Creosote	-	1.02-1.08
	Benzol	-	.88

Shale and lignite oils are generally slightly higher in specific gravity than the corresponding fractions of petroleum.

Flash Point.—The flash point is a measure of the temperature at which vapours are evolved from an oil in sufficient quantity to be dangerous.

The original method of ascertaining the flash point (still occasionally used) was to test the oil in an open dish by steadily heating, and occasionally dipping a light to the surface of the oil. As soon as a flame is observed to travel over the surface of the oil the temperature is noted. The temperature found in this way is called the open flash point. By careful standardisation of conditions reliable results can be obtained by this method. In order to attain a closer degree of accuracy and more concordant results, a special instrument has been designed by Sir Frederick Abel. This instrument and modifications of the same are now generally used for determining flash points.

The Abel flash point tester (see Fig. 21) consists of a small cup, of standard dimensions, to contain the oil. This cup is surrounded by an air space $\frac{1}{2}$ in. in thickness, around which is a water jacket. The oil cup is covered by a lid having an aperture closed by a slide, to which is attached a small lamp burning colza oil, or a small gas jet. The cover is so constructed that when the slide is moved so as to expose the surface of the oil, the flame is automatically dipped into the oil cup. A burner is provided for heating the water jacket. Both the oil cup and the jacket are provided with thermometers. In making a test the temperature of the bath and oil cup is very slowly increased, while the jet is depressed into the oil cup at frequent intervals until the flash occurs, when the temperature is noted.

This tester was officially adopted by the Petroleum Act of 1879,¹ in which the method of taking the test is fully described.

Previously to the advent of the closed flash point tester the law forbade the use of illuminating oils of a flash point lower than 100° F. by open test. This corresponds approximately to 73° F. on the closed flash point apparatus, and the latter figure is now the legal limit in this country. Open flash

¹ Full particulars can be found in Redwood's "Treatise on Petroleum."

points are generally 10° F. to 30° F. higher than the closed flash points of the same oils. The difference is caused by

the continual removal of the vapours by currents of air when using the open test.

In 1907 the use of a modified Abel apparatus for liquids of high viscosity or containing sediment was legally recognised. This form of apparatus was provided with a stirring gear to ensure perfect mixture of the sample under examination.

The barometric pressure affects the flash point, and flash points should be stated for a pressure of 30 in. of mercury. The correction is 1.6° F. for each inch of mercury in the barometric pressure.¹ A high barometric



FIG. 21.—Abel Flash Point Tester.

pressure raises the observed flash point, and vice versa.

¹ See p. 182.

The flash points of heavy oils are generally determined by the Gray or the Pensky-Marten flash point instruments. These are very similar in construction to the Abel tester, but instead of having a water jacket for the transmission of the heat, the oil cup is surrounded by a solid iron casting : between the casting and cup is an air space as with the Abel apparatus.

The design of these instruments can be observed in Figs.

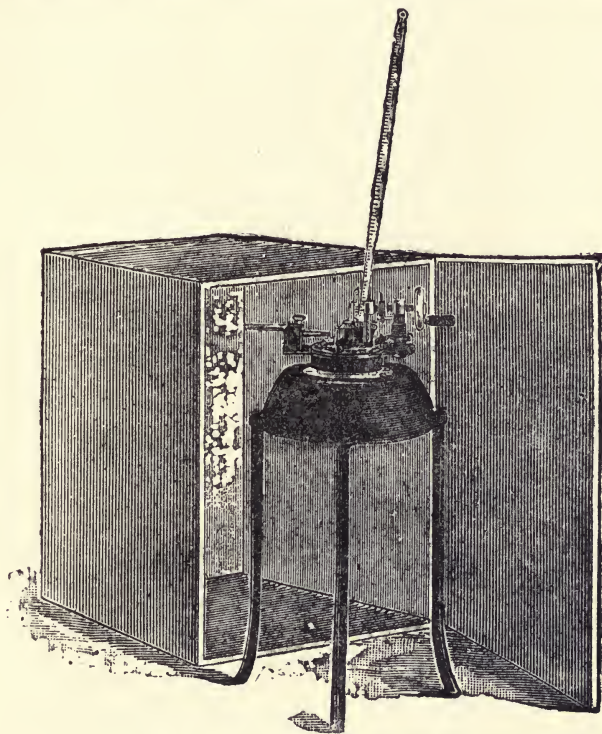


FIG. 22.—Gray Flash Point Tester.

22 and 23, the main difference between the two types being in the design of the stirring gear and the cover mechanism.

The value of the determination of the flash point is almost entirely as an indication of the danger from fire. It is of very little importance as an indication of the value of an oil for use in an engine.

Transport and storage precautions are based on flash point. Oil to be used as fuel on ships has to answer flash

point tests on account of the danger of explosion and fire from traces of oil vapours mixed with air.

Dr. Glazebrook, of the National Physical Laboratory, has made extensive investigations of the flash points of mixed oils. It is of importance to note that these are occasionally lower than the flash point of either of the oils prior to mixing.

Burning Point or Fire Test.—The burning point or fire test is the temperature at which an oil gives off a sufficient amount of vapour to maintain a flame. This temperature is ascertained by continuing the open flash point test after flashing has taken place until the vapours continue burning. When employing a closed flash point instrument it is necessary to remove the cover from the oil after the flash point has been determined, and continue the test as with the open dish.

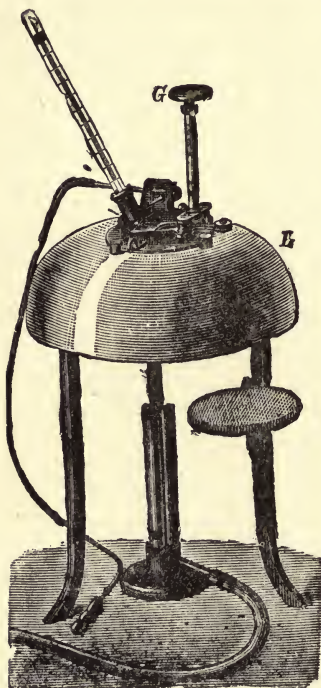


FIG. 23.—Pensky-Marten Flash Point Tester.

The determination of the burning point is not of much use, as the flash point is a better indication of the danger from fire. In the testing of fuels for internal combustion engines this property is only of passing interest. The burning point is generally 10°C. to 40°C. above the flash point.

Viscosity.—Viscosity is the resistance to change of shape. A viscous oil, or oil of high viscosity, is one which flows with difficulty; an oil of low viscosity is “thin” and flows freely.

Many varieties of instrument for measuring viscosity are used, the three most important being the Redwood viscometer used in Britain, the Saybolt instrument largely employed in the United States, and the Engler instrument which is used in Germany.

The Redwood viscometer¹ (Figs. 24 and 25) consists of a cylindrical metallic vessel provided with an agate jet at the lower end, and surrounded by a copper water jacket which allows the maintenance of a steady temperature. A ball valve is provided for the jet in order to prevent the oil from escaping during preliminary heating. A pointer indicates the correct level to which the inner vessel should be filled.

Both the jacket and the oil vessel are provided with thermometers. The outer jacket is also provided with a stirring device, and a small projecting tube at the lower edge, which tube is used for heating the contents of the jacket. The method of procedure for measuring the viscosity of an oil with this instrument is to fill the outer jacket with water (or, when high temperatures are to be used, with lubricating oil), and to pour the sample into the inner vessel until level with the pointer. The jacket is then heated to the required temperature (with high temperatures the jacket is heated slightly over the required temperature to allow for cooling) by applying a Bunsen burner to the tube which protrudes from the lower edge of the jacket. When the temperature is attained the burner is withdrawn, or adjusted as may be necessary to maintain the temperature. A 50 c.c. cylinder is now placed under the jet and the ball valve opened, when the oil flows

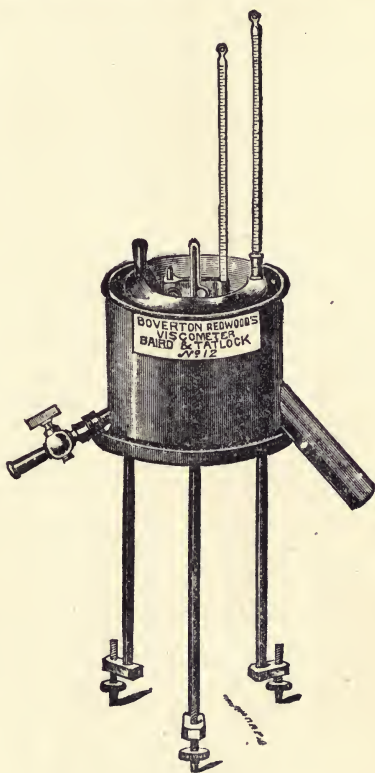


FIG. 24.—Redwood Viscometer.

¹ *Journ. Soc. Chem. Ind.*, 1886, p. 126.

through the jet into the cylinder. The number of seconds required for the discharge of 50 c.c. of oil is noted. Viscosities are frequently stated in terms of seconds, but it is better to state them in rape oil units, which are based on the viscosity of refined rape oil at 60° F., this value being accepted as 100 units. Allowance must be made in the calculation for

the specific gravity of the sample, as the pressure upon the jet is proportional to this value.

To convert the viscometer reading from seconds to rape oil units the number of seconds are multiplied by 100, divided by 535; multiplied by the specific gravity of the oil, and divided by .915. The numbers .915 and 535 are respectively the specific gravity and discharge period in seconds of rape oil at 60° F. The time occupied by the outflow of 50 c.c. of water at 60° F. is 25.5 sec.

The Engler viscometer was designed by D. C. Engler¹ for use by the German State railways.

The instrument works on the same principle as the Redwood viscometer, but

in this case a tube is used instead of a jet. The results are stated in terms of water, which is taken as unity. The Engler viscometer should discharge 200 c.c. of water in 51 to 53 sec. Each instrument requires standardisation when first used, and again after being in use for some time.

The Saybolt viscometer is similar in action to the previously mentioned instruments, but the volume of liquid discharged

¹ *Chemiker Zeitung*, 1885, 1st February.

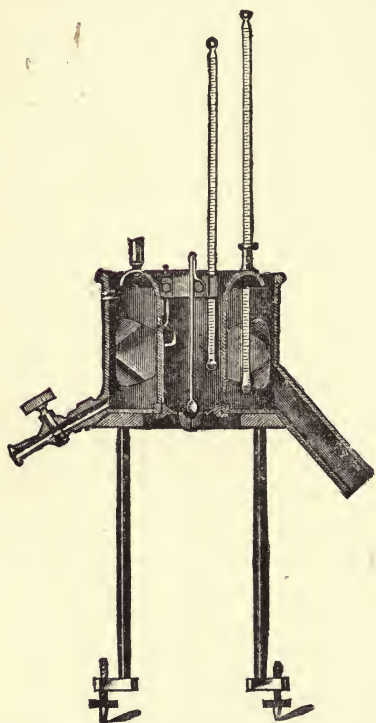


FIG. 25.—Section through Redwood Viscometer.

is indicated by the level of the oil when it reaches a glass tube which is built into the lower portion of the body of the container.

The results obtained from various viscometers cannot be translated for all oils, but their relationship is approximately shown by the following figures based upon results obtained in a number of experiments conducted in the laboratory of Sir Boverton Redwood :—¹

Redwood viscometer	-	50 c.c. at 70° F. discharge in 100 sec.	
Engler	„	- 200 c.c. at 20° C.	„ 170 „
Saybolt	„	- at 70° C.	„ 56 „

Viscosity is of considerable importance in the valuation of oils for internal combustion engines. The resistance to flow of the fuel through pipes is due to viscosity, and in deciding the diameter of service pipes this property has to be taken into account.

The majority of fuels used in carburetters are exceedingly mobile and of approximately similar viscosity, but when considering the use of some of the heavier substitute fuels (for instance, kerosene) the difference in viscosity between these and the lighter spirits is sufficient to cause a diminished rate of flow through the jet of the carburetter.

Crude petroleum, petroleum residuum, lignite tars, and coal tars possess high viscosities, and when these fuels are employed on atomising engines it is necessary to modify the area of the restricted portions of the atomising arrangements in such a way as to compensate roughly for viscosity. Distilled oils are generally much lower in viscosity than the crude oils or tars from which they are obtained. The author found from trials extending over two years on a 50 B.H.P. single cylinder Mirrlees-Diesel engine that the thermal efficiency of a Diesel engine is dependent upon the viscosity of the fuel (see Fig. 26). This fact can be explained by the assumption that viscous oils are not atomised to the same degree of fineness as more mobile oils, and that the larger globules take a longer time for combustion, thus causing late burning down the expansion curve of the indicator diagram, with accompanying decrease in thermal efficiency. From the

¹ Redwood, "Treatise on Petroleum," vol. ii., p. 280.

same series of results the author concluded that in Diesel engines the fuel consumption is very closely inversely proportional to the calorific power of the fuel, provided that other conditions are kept constant. This latter observation is equivalent to saying that the thermal efficiency is constant for fuels of various calorific powers, provided that their viscosity does not vary widely. The influence of viscosity on thermal efficiency indicates that considerable advantage is obtainable by heating the fuel.

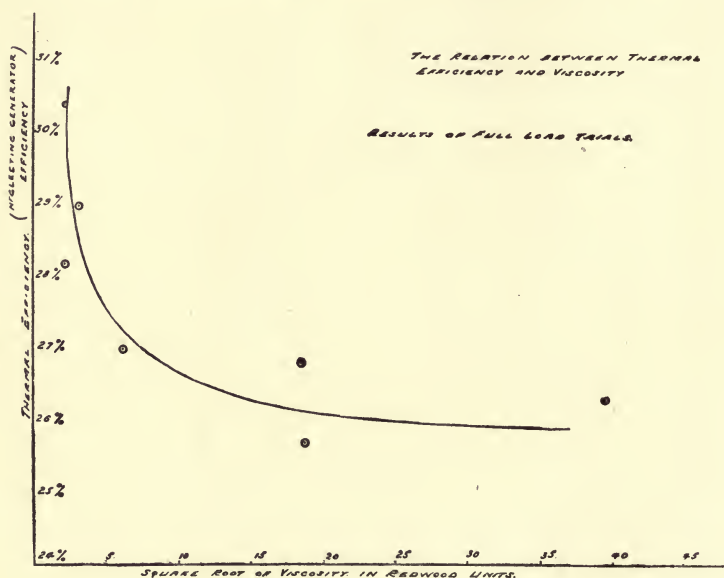


FIG. 26.

Dr. Glazebrook,¹ when investigating the viscosities of Mexican oils, observed that these values are affected by the temperature at which the oil has been maintained prior to the time of conducting the viscosity determination. He finds that if two samples of the same Mexican oil be taken, and one of them be kept cool for a prolonged period, while the other is heated for the same length of time, the viscosities of these oils, when determined at some intermediate temperature, will be different. The sample which, prior to the experiment,

¹ Dr. Glazebrook, paper read before Inst. Petr. Technologists.

has been kept at a low temperature, will be higher in viscosity than the sample which has been cooled down to the temperature of the experiment. Oils of other than Mexican origin do not exhibit this property, which is therefore available as a means of identifying a Mexican oil.

The Cold Test or Solidification Point.—In certain circumstances it is advisable to determine the temperature at which the fuel solidifies. Instruments have been designed for this purpose, but it is not necessary to attain any great degree of accuracy in the determination of these temperatures for the purposes of the internal combustion engineer.

The cold test may be taken either as the point at which complete solidification takes place, or as the point at which crystals begin to separate from the liquid. The most satisfactory test for fuel oils is to cool a boiling tube full of the oil in ice, ice-salt mixture, sodium sulphate-hydrochloric acid, or some other suitable freezing mixture. The cooling must be conducted slowly, and the oil allowed to stand without stirring, a thermometer being immersed in the oil. The effects of low temperature, for instance, the appearance of crystals (when they are discernible), or the liquid becoming buttery, or excessively viscous, should be carefully noted.

Constam and Schläpfer,¹ in their paper on fuel oils, give the results of cooling the opaque oils down to 0° C. and 15° C., and observations on the behaviour of the oils in each case. This is a satisfactory method of conducting the test when the oils are for use in internal combustion engines.

The cold test is of value in denoting the danger of freezing, or of excessive viscosity preventing the oil flowing through the tank piping and service pipes to the engine.

Benzol and some benzol mixtures are liable to solidify in exposed tanks during cold weather. Motor spirits containing naphthalene are liable to deposit crystals of the latter substance in the bottom of tanks. Light petroleum fuel oils and shale oils sometimes precipitate crystals of paraffin wax. Heavy petroleum fuels, such as Mexican and South American asphaltic crude oils and residua, become extremely viscous at low temperatures, and it becomes necessary in some cases to heat tanks which are exposed to the cold. Coal tar oils

¹ Constam u. Schläpfer, *Zeits. Ver. d. Ing.*, 1913, p. 1489.

are very liable to deposit naphthalene, and sometimes anthracene, at ordinary temperatures. As the crystals obstruct pipes, it is necessary to warm the tanks, and if filters are used it is best to arrange the heating coils so that they will melt any crystals collecting in the filters.

The Coke Test.—This value may be determined by the method of the German Tar Distillers' Federation (Deutsche Teerproduktenvereinigung), as below :—

"A platinum crucible of known weight, and measuring 22 mm. in diameter at the base and 35 mm. upper diameter, is employed. This is provided with a closely fitting lid which overlaps the upper edge of the crucible, and a hole of 2 mm. diameter is situated in the middle of the lid.

"1 gm. of oil is weighed into the crucible, and heated gently until the main portion of the oil has distilled. The flame of the Bunsen burner is now raised until it is 18 cm. long, and the crucible heated until, on testing with another burner, no flame can be observed at the hole in the crucible lid, nor is any oil discernible. The base of the crucible should be 6 cm. over the top of the burner, and during heating is held by a thin wire triangle."

Constam and Schläpfer¹ state that more concordant results are obtained when testing tars, if 1 gm. of tar be heated for seven minutes with a flame at least 20 cm. long. The crucible is 7 cm. over the burner, and held by a thin platinum triangle.

The author finds that the results of the above test give more experimental error than is desirable, the comparatively large error being probably due to the quantity of oil taken being so small. On the other hand, burning down large quantities of oil is very disagreeable on account of the large amount of smoke and soot produced. The method used in the laboratories of the Royal School of Mines makes use of the residue after the distillation test. In this way the coke on a large quantity of oil can be determined without the necessity of burning down an excessive quantity of oil. Details of this latter method are as follows :—

100 c.c. of the oil under examination are measured into a weighed Engler distillation flask, and the weight of the oil found by difference. The oil is then fractionally distilled

¹ Constam u. Schläpfer, *Zeits. Ver. d. Ing.*, 1913, p. 1489

until the temperature of vapours is 300° C. (temperature of the thermometer corrected for exposed stem).

The residue in the flask is poured while hot into a 300 c.c. silica beaker provided with a lid having a small central orifice. The distillation of the material in the beaker is then completed over a radial burner, the escaping vapours being carried off by the fume exhaust. Towards the end of the experiment the heating is greatly increased, the beaker being placed over the naked flame so that its base is at bright red heat, and the flames surround the beaker so as to form an enveloping flame bath. This is continued for one minute after all visible vapours from the residue have ceased. The beaker is now cooled, and the slight amount of condensed tar on its upper internal surface is burned off. The coke remains as a bright porous basal cake, detachable with ease from the silica beaker. It is then cooled in a dessicator and weighed. Then :—

Weight of oil used in grams - - - X.

Volume of water obtained in distillation in c.c. - Y.

Weight of coke in grams - - - A.

$$\text{Percentage of coke in dry oil} = \frac{A \times 100}{X - Y}.$$

Silica beakers are used in preference to platinum because the results obtained are found to be more consistent, and in the case of platinum there is difficulty in detaching the whole of the coke from the beaker.

This method has been used for creosote, but can be applied to other oils.

The coke value does not apply to the lighter products, and only small values are generally obtained from distillates of any description. In tar oils (creosote and anthracene oils) this value seldom reaches as much as 3 per cent. Mexican, South American, and other asphaltic petroleum crude oils and residua frequently yield over 10 per cent. of coke. The highest coke values are found in raw tars, horizontal retort tar averaging about 24 per cent., the larger part of which is free carbon. Inclined retort and coke oven tars yield low coke values (8-10 per cent.), while vertical retorts give values in the neighbourhood of 6 per cent.

Even a low coke value makes an oil unsuitable for most vaporisers, and oils of high coke value are difficult to burn

completely in semi-Diesel or Diesel engines on account of the tendency to produce coke on the walls of the combustion space (mainly on the top of piston and the exhaust valve head). Very efficient atomisation will overcome this difficulty.

Water Content.—Many methods are available for the determination of the water content of liquid fuels.¹

The more important of them may be classed as follows:—

1. Estimation by direct settling.
2. Estimation by addition of a solvent and settling treatment.
3. Estimation by addition of a solvent and centrifugal treatment.
4. Estimation by direct distillation.
5. Estimation by addition of solvent and distilling.
6. Estimation by the liberation of acetylene on adding calcium carbide.
7. Estimation by the liberation of hydrogen on adding sodium.

The first two methods are the most rapid, but are only available when the oil will settle easily; many emulsions refuse to separate even when large quantities of suitable solvents are added. When the oil weighs less than water, heating the mixture facilitates settling, as oils possess a higher coefficient of expansion than water; therefore on heating, the difference in density between the two liquids becomes greater, and promotes separation. This method of estimation is best conducted in a graduated cylinder, when, by using 100 c.c. of the sample, the volume percentage of water may be read directly.

The use of a centrifuge² facilitates the separation of the water, and is a great improvement on the direct settling method.

Direct distillation gives good results with tar oils, and tars containing moderate or small amounts of water, provided that the test is carefully conducted.

¹ I. C. Allen and W. A. Jacobs, Technical Paper 25, U.S. Bureau of Mines.

² O'Neill, "The Determination of Water and Asphaltum in Petroleum," *California Derrick*, vol. iii., June 1910, p. 3.

The standard procedure for the estimation of water in creosote is by the following method. A 250 c.c. retort provided with a long outlet tube (to act as condenser) is employed, 100 c.c. of oil being taken. The retort is held by a clamp, the jaws of which are lined with asbestos or cork. A Bunsen burner with a low flame is held under the retort, which is warmed very slowly, when the water is driven from the oil, and condenses in the side tube, falling into a 10 c.c. graduated cylinder placed under the retort outlet. When water ceases to be distilled from the sample, and no more water is observed to condense, another Bunsen burner may be applied to the outside of the tube wherever water is seen to be lying. By these means practically all the water may be driven into the cylinder. The amount of water can be read directly, or if the meniscus formed by the water and oil is irregular, a small quantity of benzol may be added, when the meniscus will flatten, and reading be made easy. The result is in volume per cent. If percentage by weight is required, 100 gm. instead of 100 c.c. of sample should be taken, and the distillate weighed.

With raw tars or crude petroleum oils containing large quantities of water the method of direct distillation is often impossible, on account of the irregular boiling (known as "bumping") which takes place. It is therefore necessary to employ some liquid which will dissolve the oil and which will carry over the water during the distillation. The method of Schläpfer¹ (a modification of Marcusson's process for the estimation of water in oils, fats, soaps, etc.) is the most suited to this test. When estimating water in heavy oils of either tar or petroleum origin the author has found the following method to yield excellent results:—

100 gm. of the oil and 200 c.c. of xylol are measured into a 500-700 c.c. conical flask and heated on a sand bath. The vapours are condensed, and 150 c.c. collected in a graduated cylinder of special design² (see Fig. 27), which allows the volume to be read to within $\frac{1}{20}$ c.c. The cylinder is suspended in a hot water bath, when, by the help of stirring with a glass rod, the water will all fall to the bottom. The volume of

¹ Schläpfer, *Zeits. f. angew. Chemie*, 1914, 27, 52-55.

² *Ibid*

water is then read by means of the graduations on the cylinder. A small loss of water takes place during this process, and for accurate results it is necessary to determine constants to compensate for this loss.

Water reacts with calcium carbide to form acetylene gas. Use has been made of this fact to estimate the water from measurements of acetylene generated by a measured quantity of oil when an excess of calcium carbide is added. The chief disadvantage of this method of determining water is the solubility of acetylene in various hydrocarbons. The solubility

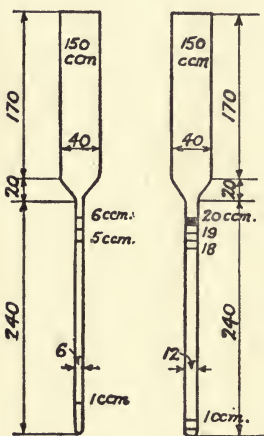
of acetylene in petroleum is not excessive (about one volume of acetylene), but in aromatic bodies the solubility is so high as to make this method of analysis useless. There is also danger of reactions with some of the compounds present in the oil interfering with the results. As the method is not generally applicable, and is only approximately correct, it is not largely used.

The reaction between water and metallic sodium results in the liberation of hydrogen, the volume of which can be measured and the water content estimated therefrom¹ (1 c.c. hydrogen represents 0.0016 gm. of water). This method is applicable to petroleum oils, in which hydrogen

is not appreciably soluble. With oils rich in compounds containing hydroxyl groups, as tar oils, this method is not reliable.

Water has also been estimated by measuring the loss of weight on heating the oil to 100° C.² This method is not accurate, and is not applicable to the majority of fuel oils.

The effect of water contained in a fuel oil depends largely upon whether the water be in solution or in suspension. If the water be in solution, as with alcohol, its action is simply one of diluting the fuel, and within moderate limits it is not an



Schläpfer tubes.

FIG. 27.

¹ Graefe, "Petroleum," vol. i., 1906, p. 813.

² Wright, *Journ. of Ind. and Eng. Chem.*, 1903, vol. i., p. 355.

objectionable constituent. Similarly the small quantity of water held in solution in some tar distillates is not objectionable except as a diluent. In whatever form water may be present it abstracts a certain amount of heat from the engine, as it leaves the cylinder in the form of steam. On this account water increases the difference between the gross and net calorific power. The amount of heat lost in this way is, however, small.

When water is present in suspension it is far more objectionable, as it causes misfiring, and sometimes will pull up an engine. When misfiring occurs on an engine fitted with a governor, the engine is heavily loaded while regaining its speed. If misfiring be frequent, the amount of unburned fuel remaining in the cylinder may become sufficient to cause a serious formation of carbon (mostly on the valve heads and the piston top), and dirty the engine. Even small quantities of water in suspension in carburetter engines cause choking at the jet, with irregular firing, and may stop the engine.

The majority of specifications for fuel oils are strict regarding the water content. The British Admiralty limit the water content of oil fuel (mainly used for boiler firing) to 0.5 per cent. The American specification by I. C. Allen¹ allows up to 1 per cent. water. The German Tar Distillers' Federation specification limits the water in tar oils for use as Diesel engine fuels to 1 per cent. The author considers that for heavy oil engine use these specifications are unnecessarily stringent and apt to increase the cost of the oil, and in a recent specification which he has drawn up for buying tar oils in this country the water content is limited to 2½ per cent.

Water is removed from fuel oil on a large scale by settling, by heating and settling, by centrifugal means, or by the "dehydrating" process. The latter method consists in distilling off the water, and then stopping the distillation. It is more expensive than the other methods. Water separates into a layer beneath petroleum and shale oils, but above tars and many tar products.

Asphaltum Content.—The term asphaltum is used to

¹ Report of the Prime Movers Committee of the National Electric Light Association, U.S.A.

signify many different substances, hence there are several entirely different methods of determining the asphaltum content, and the results obtained by each method do not in any way agree with the results obtained by other methods. Asphaltum occurs only in petroleum oils, though the term is often applied to tar products. The author prefers to determine the asphaltum content by means of the alcohol-ether method for soft asphaltum.¹ In addition to this process there is the hard asphaltum estimation,² and a method of determining the residue after prolonged heating at 300° C. Soft asphaltum is determined as follows:—

5 gm. of oil are dissolved in twenty-five times their volume of ethyl ether at 15° C. 12½ volumes of 96 per cent. alcohol are now added drop by drop from a burette, the mixture being continuously shaken. After five hours' standing at 15° C. the precipitate is separated by filtration and washed with alcohol-ether (1:2). The precipitate is dissolved from the filter paper in benzene, and collected in a tared basin. The solvent is evaporated and the hot residue washed with 96 per cent. alcohol, using 30 c.c. at a time until no paraffin wax separates from the alcohol on cooling in a test tube. After heating to 105° C. for fifteen minutes, the residue of soft asphaltum is weighed. Concordant results can be obtained by this method, if the conditions are carefully controlled.

The estimation of hard asphaltum is undertaken in the following manner:—³

2-5 gm. of an asphaltic oil, or 20 gm. of an oil which is poor in asphaltum, are weighed into a one-litre flask with forty times their volume of petrol,⁴ and the mixture well shaken. The solution is filtered, and the residue washed with petrol until the filtrate on evaporation leaves no residue of oil. The precipitate is now dissolved in benzene, and the solution evaporated at 100° C. in a tared dish. Both these tests are applied to petroleum oils, but distilled products are

¹ Schmitz, "Die flüssigen Brennstoffe," p. 131.

² *Ibid.*, p. 130.

³ *Ibid.*, p. 130.

⁴ Best quality spirit, specific gravity about '700; boiling point, 65°-95°, should be used for this purpose.

free from asphaltum, therefore the test only applies to crude oils, depetrolised crude oils, and residua.

It is common to estimate "asphaltum" by heating oil in an open dish to 300° C. until the weight of the residue becomes constant. The value obtained by this method is not comparable with the results of the previously mentioned methods of determination, but this test can be applied to any type of oil. As asphaltum is not found in distilled products, the test applies mainly to oils for use in heavy oil engines provided with atomising devices. The results of this determination are of great importance in the valuation of some classes of fuel oil. The action of asphaltic oils on engines is considered in the section on fuels for engines fitted with atomisers.

From analyses of a large number of asphaltic and non-asphaltic crude oils the author drew the following conclusions:—

1. The presence of asphaltum increases the specific gravity of oils, 1 per cent. asphaltum increasing the specific gravity by about '002.
2. Generally, asphaltic oils contain larger quantities of sulphur than non-asphaltic oils.
3. Asphaltum is generally accompanied by high viscosity.
4. Asphaltic oils are generally low in hydrogen content.

An examination of one sample of asphaltum prepared by the alcohol-ether process gave the following figures:—

Carbon	-	-	-	80·7 per cent.
Hydrogen	-	-	-	8·7 "
Sulphur	-	-	-	4·6 "
Oxygen and nitrogen	-	-	-	6·0 "
Specific gravity	-	-	-	1·065 20°/15°

Gross calorific value = 9,550 cal.; 17,190 B.Th.U. (The gross calorific power of the oil from which this sample had been extracted was 10,110 cal., or 18,198 B.Th.U.)

Samples of asphaltum obtained by the same process from different oils possess different characteristics; some are hard and brittle, whereas other samples are semi-solid, and may be pulled out into strings when slightly warmed by being held in the hand. Asphaltum is an undesirable constituent of a fuel oil, but is combustible; and asphaltic oils

can be used with success provided that suitable conditions exist on the engine.

Mechanical Impurities.—This test is undertaken on most oils in order to determine the amount of foreign matter present. The incombustible solid foreign matter is present both in the ash and in the mechanical impurities.

The following is the method which the author employs for the determination of mechanical impurities:—

20 gm. of oil are dissolved in 50 gm. of toluol and heated under a reflux condenser for five minutes. The mixture is then filtered through two counterpoised filter papers, the outer of which has had the base cut off (after folding), while the inner has been cut down from the top edge until the weights of the two are equal, as shown in sketches herewith (Fig. 28). After filtration the filters and precipitate are dried in a steam oven at 105° C.

By placing the outer filter on the right-hand pan, and the inner one on the left-hand pan of the balance, and then adding weights until they are balanced, the correct weight of the mechanical impurities is obtained.

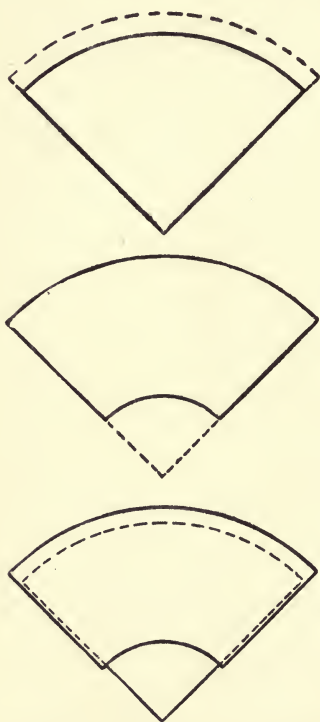


FIG. 28.—Inner Cone, Outer Cone, and Complete Filter.

Mechanical impurities are often found in crude petroleum and consist mainly of earthy matter. Among the fuel oils which are sold by well-known companies in this country one rarely finds more than minute traces of mechanical impurities. Raw coal tars are not tested for mechanical impurities, as free carbon is present in such quantity as to entirely outweigh the former value.

Free Carbon.—This substance is best determined by Köhler's¹ method :—

10 gm. of tar are mixed with 25 gm. of glacial acetic acid and 25 gm. of toluene and boiled in a conical flask, under a reflux condenser. The mixture is filtered through two counterpoised filters (see p. 122), and the precipitate washed with hot toluol until the washings become colourless. The precipitate is then dried at 120° C., the filters separated, and the difference of weight between the filters noted.

Constam and Schläpfer² examined two samples of "free carbon," and found that this body contains other elements than carbon :—

	Carbon.	Hydrogen.	Oxygen and Nitrogen.	Gross Calorific Value.
	Per Cent.	Per Cent.	Per Cent.	Cals.
First sample - -	92.7	2.6	4.0	8,271
Second sample - -	91.6	2.6	5.1	8,218

Free carbon is a fine dust carried over from the retorts during the carbonisation of coal. The estimation of this body is of the greatest importance when examining raw tars for use in Diesel engines. In other fuels free carbon seldom occurs. Many attempts have been made to extract this substance from tars. The author has been able to separate it by filtration, both in laboratory experiments and on a small commercial scale. Müller³ was able to extract about two-thirds of the free carbon from certain tars by means of a centrifugal separator. Tars containing considerable quantities of free carbon have been burned in Diesel engines, but the action of this body on the exhaust valves necessitates frequent examination and grinding. Tars from vertical retorts containing less than 4 per cent. of free carbon have been used on Diesel engines without much difficulty being experienced,

¹ "Lunge Berl.," vol. iii., p. 385.

² *Zeits. Ver. d. Ing.*, 1913, p. 1489.

³ Müller, *Journ. f. Gasbeleuchtung*, 1912, p. 229.

and are at present in use in Germany on a large scale. Free carbon contents of over 6 per cent. are generally found to make fuels unsuitable for internal combustion engines.

Ash.—The ash is generally estimated by burning 10 gm. of the oil in a tared platinum dish, then repeatedly igniting the residue to a red heat and weighing till the weight becomes constant. Constam and Schläpfer¹ advocate taking 50 gm. of the oil, thus increasing the accuracy of the test. After weighing it is advisable to examine the ash by rubbing between the fingers, whereby it is possible to distinguish between ashes which are soft and comparatively harmless and ashes which are abrasive and likely to cause wear on the working parts of the engine.

The ash content of a fuel is naturally of great importance, as this substance, if present in only a small proportion, will collect in the cylinder and have a very deleterious action on the piston rings, cylinder walls, exhaust valve face, and exhaust valve seat. Distilled fuels should be entirely free from ash, and heavy residue should never give a higher ash content than 0.05 per cent. The greatest difficulty is experienced in burning heavy oils containing over 0.10 per cent. of hard and gritty ash. Soft ashes, such as sodium sulphate (which is often present in tar products which have been washed for the removal of tar acids), may be present in fuels for heavy oil engines to the extent of as much as 0.20 per cent. without causing trouble.

Fractional Distillation.—It is frequently desirable to know the boiling points of the various constituents of a liquid fuel. These are best determined by distilling a sample of the fuel and observing the proportion distilled at various temperatures. Considering a sample of crude oil yielding 10 per cent. of distillate at 150° C., we should know that roughly 10 per cent. of fuel suitable for refining into motor spirit was present in the same. If, then, further distillation yielded an additional 25 per cent. from 150° C. to 300° C. this would indicate the presence of approximately 25 per cent. of unrefined kerosene or paraffin oil. From the distillation test information is obtained regarding the boiling point of the compounds present in a liquid fuel. Thus a mixture of a

¹ Constam u. Schläpfer, *Zeits. Ver. d. Ing.*, 1913, p. 1489.

light and heavy product may be distinguished from a medium product, and the quantities of each product present in the mixture determined.

The results of fractional distillation are greatly influenced by the type of apparatus employed. The three most important methods of fractional distillation are by retort, by distillation flask, and by means of a flask and dephlegmator.

Distillation by Retort.—This method finds use in the testing of commercial benzols and several other coal tar distillates. It differs from other methods mainly in the fact that the bulb of the thermometer is immersed in the liquid. The results obtained from this test vary according to the position of the thermometer, and the size of retort and condenser, no special dimensions having been adopted as a standard.

Stavely¹ suggests the following procedure which yields satisfactory results :—

The distillation takes place from a 6-oz. stoppered retort (benzol retort), which is connected to a Liebig condenser, the inner tube of which is 30 in. long and 1 in. in bore. 100 c.c. of the liquid is taken for the test. The bottom of the thermometer should be situated $\frac{3}{8}$ in. from the base of the retort. The retort is heated by a rose Bunsen burner, and the distillation conducted at such a speed that the drops from the end of the condenser fall separately.² The distillate is collected in a 100 c.c. burette. The burner is turned off before the thermometer reaches the desired temperature, so that the correct degree is not exceeded, and the quantity of distillate read off when the condenser has drained. If only rough results are required (as is frequently the case in fuel testing), it is not necessary to stop the distillation, but an allowance for the contents of the condenser can be added to the volume of the distillate. At the end of the test the residue is added to the distillate, and any shortage of the total volume is added to the volume of the distillate.

Allen³ employs a 200 c.c. (8 oz.) tubulated retort, and notes that variations in the dimensions of the thermometer

¹ *Chemical News*, xliii., p. 70.

² A speed of two drops per second has been found most satisfactory.

³ "Commercial Organic Analysis," 2nd edition, ii., p. 496.

yield large differences in the results. He states that variations rarely exceed 1 to $1\frac{1}{2}$ per cent. if the test is properly conducted. "Bumping" or spasmodic boiling of the liquid when distilling can be prevented by placing a piece of porous tile in the retort before heating the oil. Porous tile should never be added to the oil when hot, as the resulting violent ebullition is liable to burst the flask. The results of a retort test cannot be directly compared with results obtained by other forms of distilling apparatus, as the immersion of the thermometer bulb gives the temperature of the residue,

which with liquids of mixed composition is considerably above the temperature of the vapour.

Distillation by Engler Flask.—Petroleum oils are tested with the Engler flask, which is a distillation flask of the dimensions shown in the accompanying sketch (Fig. 29).

The top of the bulb of the thermometer should be situated on a level with the bottom of the side tube. The

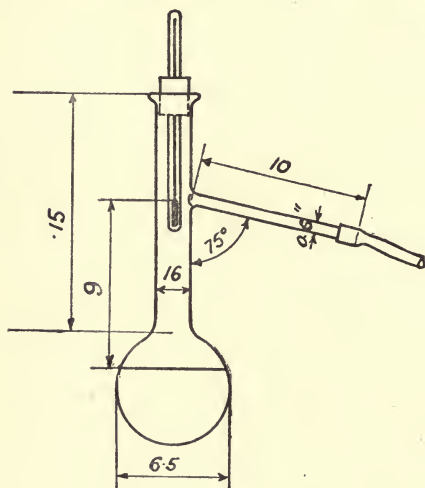


FIG. 29.—Engler Flask.

flask is connected to a condenser, 100 c.c. of the sample are taken, and a little porous tile added to prevent irregular boiling. The distillation is conducted at the rate of two drops per second, and the flame removed, allowing the condenser to drain before the distillate is measured. A protecting shield is required to prevent draughts from affecting the flame. The distillate may be measured by volume or by weight, the former being much the more rapid method.

Ubbelohde¹ uses the apparatus shown in Fig. 30, and employs 100 c.c. of oil (with oils of very high boiling point

¹ Holde, "Untersuchung der Kohlenwasserstofföle u. Fette," p. 32.

80 c.c. can be taken). The oil is slowly heated to boiling point, and the "drop point" noted when the first drop of distillate falls from the condenser. The distillation is maintained at a speed of two drops per second, a pendulum which swings twice per second being attached to the condenser clamp. The fractions are collected at 150° C., 200° C., 250° C., 275° C., and 300° C., and readings of the volume of distillate are taken at the nearest $\frac{1}{2}$ per cent.

Distillation by Flask and Dephlegmator.—Dephlegmators

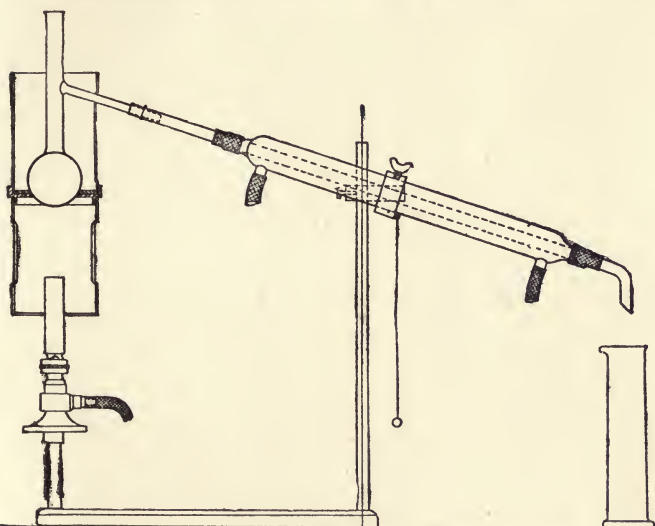
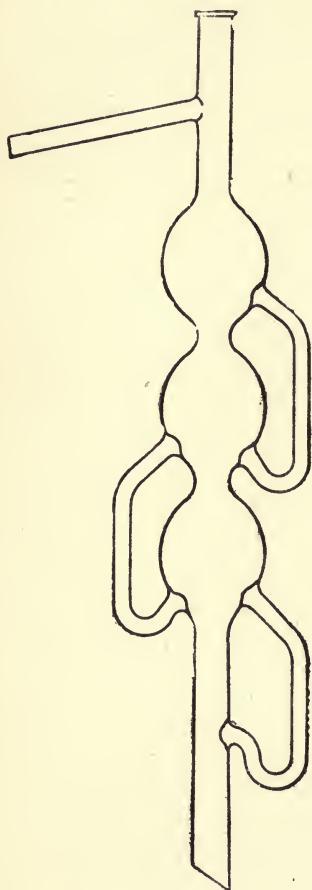


FIG. 30.—Engler-Ubbelohde Apparatus.

or fractionating columns are used with a view to obtaining a finer degree of fractionation of the oil under test, that is to say, a more complete separation of the various constituents present.

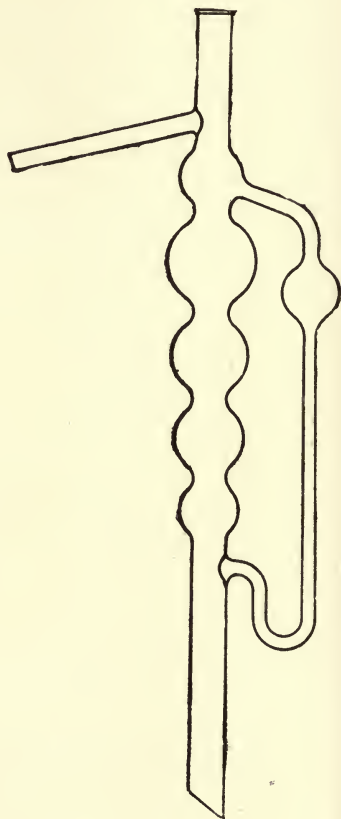
Suppose that a mixture were made of equal quantities of two liquids which are soluble in each other, one boiling at 100°, and another at 150°. Now if these were distilled from a flask until one-half of the mixture had passed over, it would be found that the distillate consisted mainly of the lighter product, but contained a certain quantity of the heavier product. Similarly the residue would consist mainly of the heavier constituents boiling at 150°, but would contain

some of the liquid which boiled at 100° . By employing a dephlegmating column the heavier product would be much more effectively removed from the vapour during distillation.



LE BEL - HENNINGER DEPHLEGMATOR.

FIG. 31.

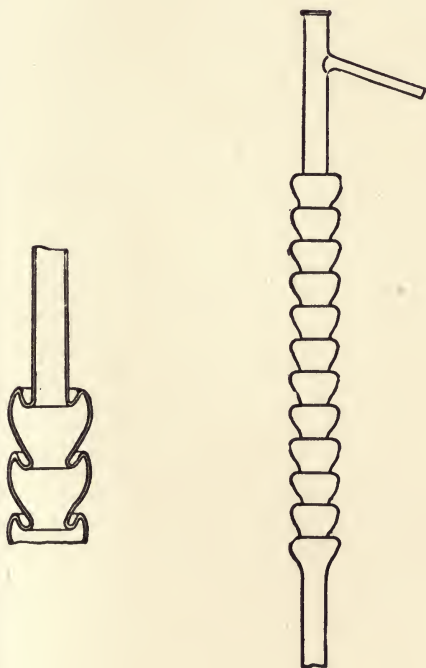


GLINSKY DEPHLEGMATOR.

FIG. 32.

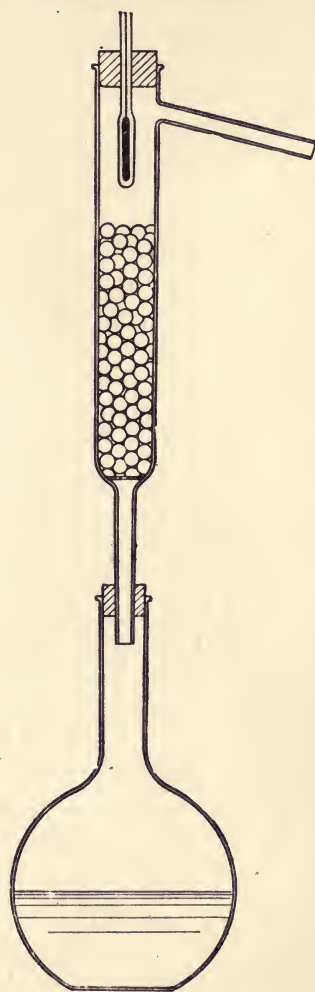
The effect would therefore be that the distillate would be almost entirely the product of lower boiling point, whereas the residue would consist almost entirely of the liquid of higher boiling point. The reason for the incomplete

separation of the constituents of a mixture when subjected to distillation is explained by a study of the effects of their



FRACTIONATING COLUMN (YOUNG)

FIG. 33.



BEAD COLUMN DEPHLEGMATOR.

FIG. 34.

vapour pressures. Consider the case of a mixture of two liquids undergoing distillation at normal pressure. The sum of the vapour pressures exerted by the two constituents is

equal to the atmospheric pressure. The composition of the vapour immediately over the surface of the liquid will therefore be such that the amount of each constituent present will be proportional to the vapour pressure exerted by that constituent. If the mixed vapours are passed through a dephlegmator, an absorption of the higher boiling point constituent takes place in the condensed mixture which is present in the dephlegmator, thus leaving vapours containing a higher proportion of the lower boiling constituent.

Liquid fuels are nearly all mixtures of large numbers of chemical compounds, and if it is desired to obtain a close insight into the nature of their constituents it is often advisable to employ a dephlegmator. Dephlegmators are, however, not suited for use with high boiling oils, and therefore are mainly employed for testing motor spirits. High boiling products are almost certain to undergo a process of cracking if distilled through a dephlegmator.

Three common forms of dephlegmator, or fractionating column, are shown in the accompanying diagrams (Figs. 31, 32, and 33).

Garry and Watson¹ have tested the fractionating properties of two dephlegmators, and compared the results obtained from a plain distillation flask, as follows:—

	First Drop Condensed at	Volume per Cent. of Fractions.						
		To 70 deg. C.	70-80 deg. C.	80-90 deg. C.	90-100 deg. C.	100-110 deg. C.	110-120 deg. C.	120-140 deg. C.
Plain distillation flask side tube, 9.4 cm. up	63° C.	0.5	3.5	40.0	32.0	16.0	5.0	2.0
Le Bel-Henniger's dephlegmator, 3 bulbs	58° C.	2.0	17.0	26.0	30.0	15.0	4.0	4.0
Glinsky's dephlegmator, 5 bulbs	58° C.	1.0	12.0	35.0	28.0	15.0	4.0	4.0

The procedure when employing a dephlegmator is similar to that adopted when using an Engler flask, but it is advisable to take a larger quantity of the sample for testing. The thermometer bulb is situated slightly below the outlet at the

¹ *Journ. Soc. Chem. Ind.*, 1904, p. 704.

top of the column. A plain column filled with glass beads or broken glass makes a very effective dephlegmator (see Fig. 34).

The author generally employs both the Engler flask and the retort on high boiling products. Fractionating columns are liable to cause cracking at high temperatures. For fuels for

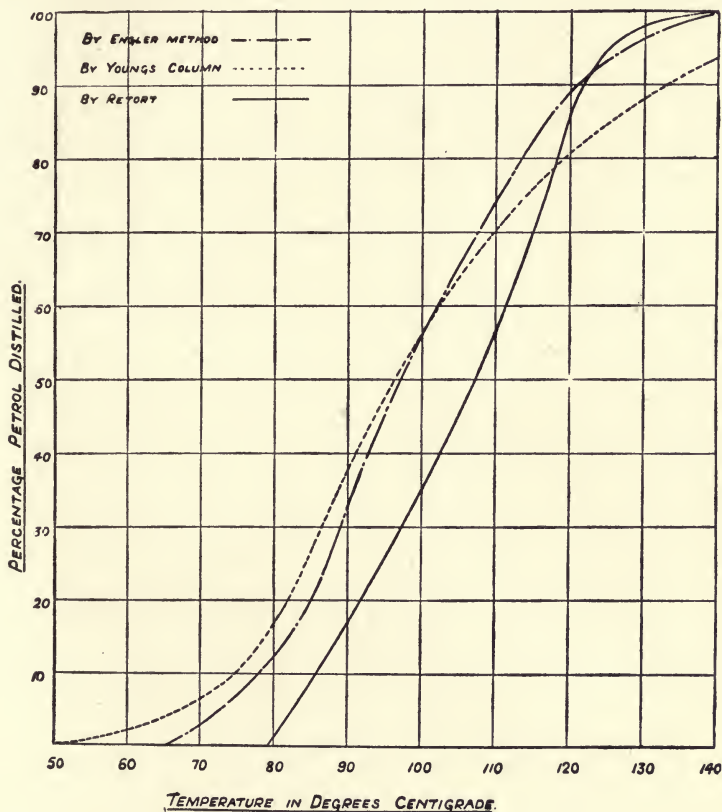


FIG. 35.

carburetted engines it is, however, best to use a dephlegmator and to take 200 c.c. of the sample for this test. The results obtained by any one of these tests differ greatly from those obtained by other methods. The results of distillations are best recorded in graphic form, and with practice it is possible to form an opinion of the distilling properties of an oil at a

glance (see accompanying diagrams). Fig. 35 shows three distillation curves obtained by different types of apparatus from the same motor spirit. In the diagram (Fig. 36) three graphs obtained by retort, Engler flask, and Le Bel-Henniger dephlegmator distillations of a mixture of equal parts of commercial benzol, toluol, and xylol are shown.

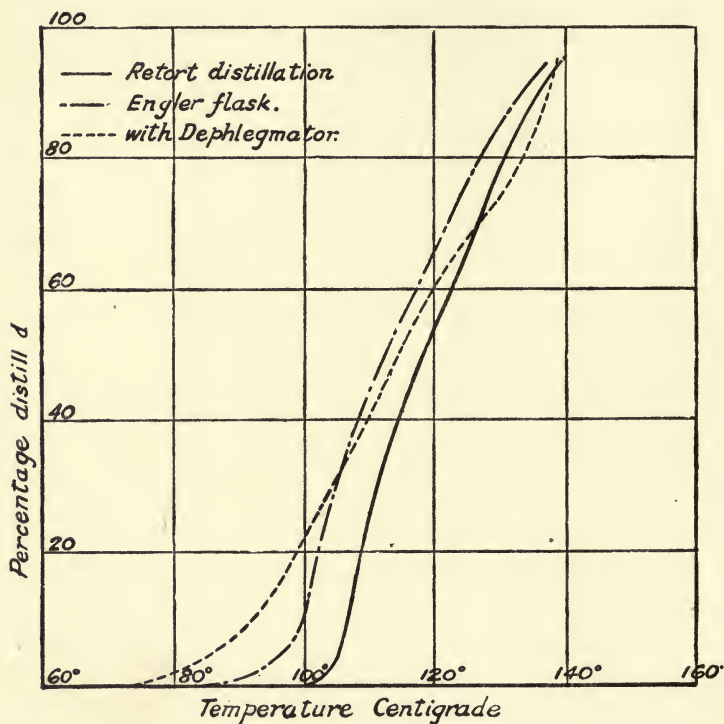


FIG. 36.—Distillation of Mixture of Benzol, Toluol, and Xylol.

Many special forms of apparatus have been designed for special tests. The distillation tests adopted for raw tars with a view to their valuation for distilling purposes are conducted on much larger samples, and copper vessels are frequently used. The water contained in many raw tars makes distillation very irregular, and there is danger of glass vessels being broken by the bumping which takes place.

The Combustion or Ultimate Analysis of Liquid Fuels

—When it is necessary to determine the quantitative ultimate composition of a fuel the combustion method is employed. This is the analytical process used for the ultimate analysis of all organic substances. Though the process is simple in theory the manipulation is difficult, so that both extreme care and considerable experience are required in order to obtain accurate results. A full account of the theory and practice of this determination will be found in any text-book of organic chemistry. The combustion determines the carbon and hydrogen present in a substance, and providing that the sulphur content is known, and that other elements are absent, the oxygen content can be calculated by difference.

The process consists in burning a weighed quantity of the substance in a tube, then collecting the water and carbon dioxide formed by the combustion in weighed vessels containing absorbing materials. The increase in weight of these vessels represents the water and carbon dioxide formed, and from these data the hydrogen and carbon contents of the substance can be calculated.

The substance to be analysed is burned in a tube of hard glass or silica about thirty inches long and half an inch in bore. The tube is heated by a special combustion furnace. The apparatus is shown in Fig. 37, and is so arranged that either air or oxygen can be admitted to the furnace from A into wash bottle B, which contains sulphuric acid and serves as a drying agent. After passing through the sulphuric acid the air or oxygen is passed through the towers C and D, where any carbon dioxide is removed by means of solid potassium hydroxide. The air or oxygen, now purified, is led into the combustion tube in the furnace, where it passes over a coil of oxidised copper gauze E, which serves to prevent the volatile products of distillation from passing backwards in the tube. After E is placed a small porcelain or platinum boat F, which contains the substance to be burned. The products of combustion are then passed through heated copper oxide G to ensure complete oxidation. A large porcelain boat H containing lead chromate is placed near the end of the tube to remove sulphur from the products of combustion. As the nitrogen contained in the compound

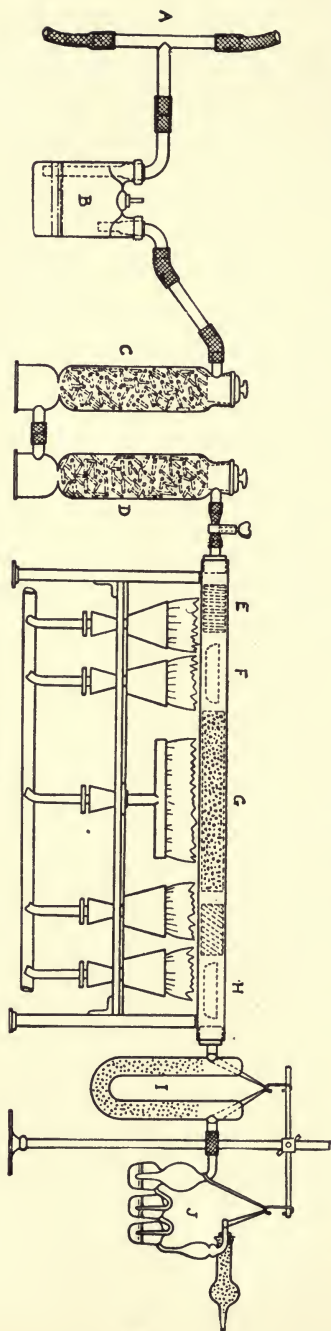


Fig. 37.—Combustion Apparatus.

is frequently oxidised in the combustion furnace, a spiral of copper gauze is placed in the end of the tube in order to decompose any oxides of nitrogen which may be formed. The products of combustion are next passed through a calcium chloride tube I, which extracts the water, and thence through a potash bulb J, containing a 40 per cent. solution of caustic potash which absorbs carbon dioxide. Before use the apparatus must be carefully examined to ensure all the joints being gas tight, and the furnace heated for a period of several hours to remove completely water and dust from the tube. The front portion of the tube is then allowed to cool, the calcium chloride tube and the potash bulb weighed, and about 1.5 gm. of the oil weighed into a boat and passed into the furnace tube. The copper oxide coil is replaced and air slowly passed from a gas holder through the train. The front end of the tube is then heated until the copper oxide coil is glowing, care being taken not to distil the oil from the boat until the coil is at a red heat. By slowly warming the tube in the neighbourhood of the boat the oil may now be burned, but the rate of burning must

be very slow, and the speed of air such that about one bubble per second passes through the first bulb of the potash absorption vessel. When the oil is nearly completely distilled the flame may be raised until the portion of the tube which surrounds the boat is at a bright red heat. Oxygen is then passed through the tube for half an hour to complete the combustion, after which air is passed through for an hour to wash out any carbon dioxide lying in the tube and to replace the oxygen in the absorption tubes.

After cooling the absorption vessels they may be weighed. The entire analysis requires at least six hours, and attempts to hasten the process only lead to failure. The weight of hydrogen in the oil is calculated from the increase in weight of the calcium chloride tube by multiplying by $\cdot 1119$. The carbon in the oil is calculated by multiplying the increase in weight of the potash bulb by $\cdot 2727$.

As the combustion is a difficult and lengthy procedure, and is generally not essential to the valuation of a liquid fuel, it is only carried out in special cases. The elementary composition of a fuel does not vary greatly among oils of the same chemical type. Provided that the origin and specific gravity of a liquid fuel be known, it is generally possible to estimate the hydrogen content with a fair degree of accuracy. The combustion is frequently undertaken in order to allow the calculation of net calorific powers from the gross calorific powers obtained by the calorimeter. The author has found that for heavy coal tar products and petroleum oils the difference between the gross and the net calorific values can be obtained with a sufficiently close degree of accuracy from the specific gravity, by means of the curves shown in Fig. 38, which have been obtained from past experience with oils of these types. The curve of lower specific gravity indicates the values for petroleum products, and the curve of higher specific gravity those for coal tar products.

When oils are of doubtful chemical type, that is, neither mainly aromatic (as obtained by high temperature destructive distillation of coal) nor of pure petroleum origin, it becomes necessary to undertake a combustion in order to obtain (from the hydrogen content) an estimate of the proportion

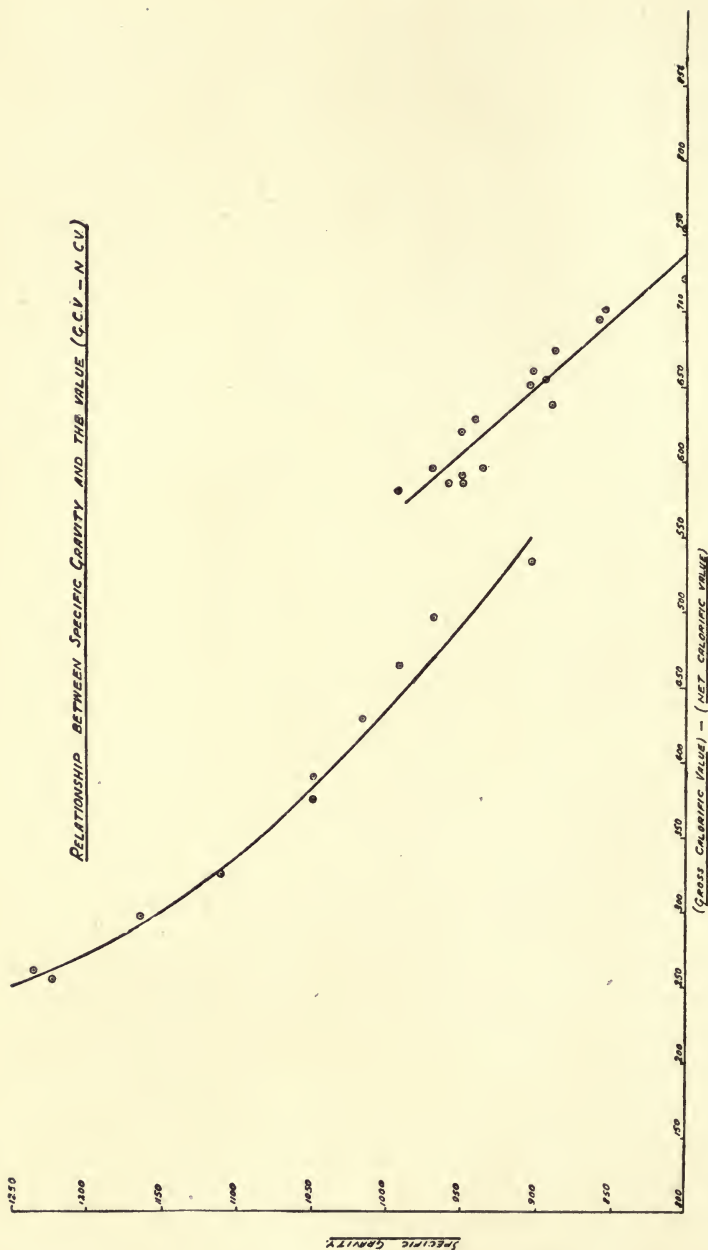


FIG. 38.

of compounds of each type present. Even in this case the experienced analyst can form a rough estimate by comparing the distillation curve with the specific gravity, but this latter method of estimating the composition requires the previous collection of data from a large number of varying samples of oil.

The proportions of carbon, hydrogen, and oxygen present in a fuel indicate the amount of air necessary for its combustion, and, to a small extent, show the likelihood of carbon deposits being formed in the engine, fuels of high hydrogen content being least liable to carbonise. With oils for Diesel engines low hydrogen content is accompanied by ignition difficulties, as oils poor in hydrogen have generally high spontaneous ignition temperatures.

Sulphur Content.—When the heat value of a liquid fuel has been determined in a bomb calorimeter, the sulphur remains, as sulphuric and sulphurous acids, in the condensed liquid at the bottom of the bomb. The determination of sulphur from this liquid is much simpler than by other methods. When a sulphur estimation is to be undertaken, it is advisable to include 10 c.c. of water in the bomb, and to employ a pressure of 30 atmospheres. The bomb is washed out with distilled water, the washings being collected in a beaker. Bromine water is added (to oxidise the sulphurous acid) and the solution boiled until excess of bromine has been expelled. The liquid is then filtered, the filtrate heated to boiling, and a hot solution of barium chloride added. After standing for twelve hours the precipitate of barium sulphate is removed by filtration, ignited, and weighed (factor for sulphur in barium sulphate, '137). Patterson¹ estimates the sulphur in the bomb liquor by titrating the total acid with standard barium hydrate after expelling CO₂ by boiling, using phenolphthalein as indicator; then adding 10 c.c. of decinormal sodium carbonate solution, filtering off barium sulphate and carbonate, and titrating back the filtrate with decinormal hydrochloric acid, using methyl orange as indicator. The sodium carbonate used (calculated from hydrochloric acid used) gives the barium nitrate, hence the nitric acid. From the difference between the barium hydrate and the sodium

¹ Private communication.

carbonate neutralised, the sulphuric acid present in the bomb liquor may be calculated.

Sulphur in oil may also be determined by a modification of the fusion method which is used for the estimation of sulphur in solid fuels. Tinkler and Challenger¹ give the following procedure for heavy oils:—

From .75 to 1.5 gm. of the oil are weighed into a very small platinum crucible which contains about 4 gm. of a mixture of pure dry lime and sodium carbonate in the proportion of four parts of the former to one of the latter. The contents of the crucible are then thoroughly mixed by means of a thin glass rod, and the crucible filled with more of the mixture, during which process any oil adhering to the glass rod is completely removed. A large platinum crucible is then inverted over the smaller one, so that the top of the latter is in close contact with the bottom of the former. The whole is then inverted, and more of the mixture of lime and sodium carbonate placed in the larger crucible until the smaller one is just covered.

A piece of thick asbestos millboard is placed over the larger crucible, and the whole transferred to a previously heated muffle furnace. Owing to the presence of the asbestos the oil does not become hot until the mixture of lime and sodium carbonate is already heated. After five minutes the asbestos is removed, and the heating continued for two hours.

The contents of the crucible are afterwards dissolved in hot water, and any remaining sulphides or sulphites oxidised by the addition of bromine water. The solution is filtered, the filtrate acidified with hydrochloric acid, boiled until colourless, and the sulphate precipitated with barium chloride. The sulphur content of the oil is calculated from the weight of barium sulphate precipitated.

The sulphur content of light liquid fuels may be determined by burning in a lamp and determining the sulphur in the products of combustion. By this method a portion of the sulphur remains in the wick of the lamp, which necessitates a fusion and correction.²

A modification of the combustion apparatus used for the

¹ Tinkler and Challenger, "Chemistry of Petroleum," 1915, p. 172.

² United States Bureau of Mines, Technical Paper 26, p. 16.

ultimate analysis may be employed for sulphur determination, in which case the oil is burned in oxygen at atmospheric pressure, and the sulphur determined in the products of combustion. Another method is to oxidise the oil with fuming nitric acid in a sealed tube (Carius method), but this procedure is lengthy, difficult, and not always satisfactory.

The corrosive action of sulphur contained in liquid fuels has been greatly exaggerated. Experience has shown that the products of combustion of fuel oils rich in sulphur do not cause corrosion at high temperatures. The author has frequently run engines on oils containing over 3 per cent. of sulphur, and has never been able to note any effects on the engine parts which could be caused by this constituent. Exhaust pipes and silencers which are at comparatively low temperatures are sometimes affected by the sulphuric acid formed in the exhaust, but parts which are maintained at a temperature over 150° C. do not allow the condensation of these acids, and are therefore not affected. Petroleum oils which are high in sulphur, *e.g.*, heavy Mexican fuel oil, are liable to wear the faces of the exhaust valve and exhaust valve seat, but the action is due to the asphaltum content of these oils, and not directly to the sulphur. The asphaltic petroleum oils are frequently of high sulphur content. Light Mexican fuel oil (sp. gr., .910), though comparatively rich in sulphur, is low in asphaltum content, and does not wear the exhaust valve face to any appreciable extent.

As the sulphur in an oil leaves the engine in the form of sulphur dioxide, the exhaust naturally smells strongly when running on oils of high sulphur content. This is an objectionable feature with fuels for road vehicles, but is of minor importance in larger engines where the exhaust is discharged at a considerable height from the ground. Apart from the corrosion of silencers, which is very rare, and from the odour of the exhaust, there are no appreciable drawbacks to the use of liquid fuels of high sulphur content.

Naphthalene Content.—The estimation of naphthalene is of importance when analysing the higher boiling distillates of coal tars. It is rarely necessary to make an estimate of this substance, but its presence is noted by its influence on the cold test. Naphthalene in oils can be best determined

by fractionating and collecting the distillate 200° C. to 260° C., then cooling to 15° C. for twenty-four hours to allow crystallisation to take place. The crystals are then filtered off and adhering oil removed by pressing between filter papers, after which the naphthalene may be weighed. This method, though only approximate, is sufficiently accurate for the purposes of fuel testing.

Naphthalene is an aromatic hydrocarbon possessing the formula $C_{10}H_8$. It is rich in carbon, and only contains 6.2 per cent. of hydrogen, and therefore burns with a smoky luminous flame. The pure hydrocarbon possesses a gross calorific value of 9,668 cal. per gram, melts at 79° C., boils at 218° C., and possesses a sp. gr. of 1.145. Naphthalene possesses the property of subliming, of which use is made in its commercial purification.

As a constituent of heavy fuel oils naphthalene is liable to cause obstruction of the fuel pipes, and has been associated with the formation of deposits in the atomising devices of Diesel engines. Apart from these difficulties, which may be overcome by mechanical means, naphthalene possesses valuable fuel properties. In normal times it is available in considerable quantities at reasonable prices. Oils containing crystals of naphthalene require heating in order to completely liquefy them before passing into the engine.

Crude naphthalene is obtained from the heavier coal tar distillates by draining or by means of a centrifuge. Special engines of the Diesel type have been designed for burning crude naphthalene, warming spaces for melting the crystals being heated by the cylinder circulating water. On account of the high carbon content and heat value it is frequent to add refined naphthalene to some of the mixtures which have recently been sold for motor spirit. Naphthalene may assume much importance as a constituent of motor spirits if the use of alcohol becomes more common, as the latter fuel is very deficient in carbon.

Anthracene Content.—It is not usual to estimate anthracene in fuel oils, though it is a component of most of the heavy distillates of coal tar. The anthracene content may be determined by collecting the distillate boiling 270° C. to 300° C., and cooling and filtering, whereby crude anthracene

is obtainable. The proportion of the pure compound present in the crude product may be determined by oxidation with chromic acid in the presence of glacial acetic acid, whereby anthraquinone is produced. This test is known as the Höchst test.¹

Anthracene is seldom present in fuel oils in such quantities as to cause obstruction to the pipes, and is of little importance as a fuel. Pure anthracene possesses the empirical formula $C_{14}H_{10}$, melts at $213^{\circ} C.$, boils at $360^{\circ} C.$, and possesses a sp. gr. of 1.147. It is an aromatic hydrocarbon, and contains only 5.6 per cent. of hydrogen.

Tar Acids.—Coal tar distillates frequently contain acidic bodies, mainly phenol or carbolic acid (formula C_6H_5OH) and the three isomeric cresols (formula $C_6H_4CH_3OH$). These and other similar compounds are included under the term "crude tar acids." They may be estimated by washing the oil with caustic soda ($40^{\circ} Tw.$) in a separating funnel, and then withdrawing the bottom layer, which will be a solution of the sodium salts of these tar acids. To this solution is added 25 per cent. sulphuric acid, when the free tar acids rise to the surface of the resulting sodium sulphate solution, and can be measured directly.

Tar acids are sometimes found in small traces in benzol, but they are never present in such quantities as to affect the value of this product as a fuel. In the heavier tar oils used for Diesel engines the tar acids do not affect combustion, but their heat value is considerably below that of the bulk of the oil, and their presence is, therefore, accompanied by low calorific powers. The author found the calorific power of a creosote containing 10 per cent. of tar acid to be 9,255 cal. (16,659 B.Th.U.). After removal of the tar acid by washing, the remaining oil possessed a calorific power of 9,501 cal. (17,102 B.Th.U.). The removed acids showed a calorific value of 7,995 cal. (14,391 B.Th.U.).

Tar Bases.—Distillates of coal tar in the crude state contain basic bodies. The basic compounds are mainly pyridine, quinoline, and isoquinoline, each of which contains one atom of nitrogen in the molecule. The effect of the presence of tar bases on the running of engines is not noticeable, and they burn

¹ See Lunge, "Coal Tar and Ammonia," 1916, p. 634.

quite satisfactorily. These substances are sometimes used for the denaturing of alcohol, that is to say, they are added to alcohol in order to make the spirit unsuitable for drinking.

They can be estimated in tar oils by washing the oil with 25 per cent. sulphuric acid, separating, and neutralising the separated sulphuric acid compounds by the addition of caustic soda, when the free bases will separate as a precipitate.

The Temperature of Spontaneous Ignition. — The temperature at which a fuel, when surrounded by an atmosphere of oxygen or air at the same temperature, will ignite without the application of any local high temperature (*e.g.*, an electric spark, or a flame), is known as the temperature of spontaneous ignition, and, in connection with fuels for internal combustion engines, is of fundamental importance. It has no connection with the flash point or burning point. The determinations of the temperature of spontaneous ignition of fuel oils have been made by Holm¹ and by Constam and Schläpfer,² and by the author. Holm employed a vertical tube furnace, the determinations being made by dropping the substances on to a heated porcelain crucible cover, the temperature being measured by a thermocouple pyrometer. The results were of the greatest interest, and are therefore given here:—

TEMPERATURES OF SPONTANEOUS IGNITION IN OXYGEN, OBSERVED BY HOLM

	Deg. C.		Deg. C.
Hydrogen - - -	470	Ethyl ether - - -	400
Petrol - - -	415	Acetaldehyde - - -	380
Paraffin - - -	380	Ethyl alcohol - - -	510
Gas oil - - -	350	Acetone - - -	570
Roumanian residuum -	380	Benzene - - -	520
Machine lubricating oil -	380	Xylene - - -	500
Compressor lubricating oil -	410	Aniline - - -	530
Paraffin oil (from lignite) -	370	Cellulose - - -	360
Paraffin wax - - -	310	Anthracite - - -	440
Tar oil - - -	530		

¹ Holm, "Ueber Entzündungstemperaturen (Zündpunkte), besonders von Brennstoffe," *Zeit. für angew. Chemie*, 1913, p. 273.

² Constam u. Schläpfer, *Zeits. Ver. d. Ing.*, 1913, p. 1489.

Constam and Schläpfer publish the analyses of 220 fuel oils, the temperature of spontaneous ignition having been determined in each case. They also undertook experiments regarding the effect of various heating surfaces on the ignition temperatures, and made duplicate experiments in atmospheres of oxygen and air. The apparatus employed for these experiments is shown in the accompanying diagram, Fig. 39.

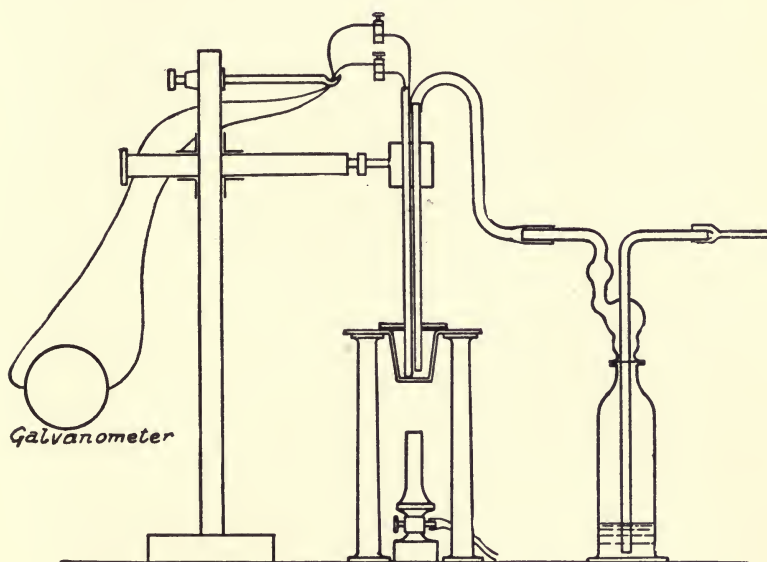


FIG. 39.

The majority of the determinations were made in a platinum crucible with an atmosphere of oxygen.

In order to obtain a uniform temperature in the heating space, a small platinum crucible was placed inside a larger crucible, and the intervening space of about 3 mm. was packed with ignited sand. The crucible was covered with an asbestos lid in which were holes to allow the passage of a platinum-rhodium thermocouple, and a tube to supply oxygen. The outer crucible was heated by a small Bunsen burner, and the oxygen slowly passed into the inner crucible. The thermocouple was protected by a thin tube, the lower end of which

was situated 3 mm. above the base of the crucible (Fig. 40). Raising the thermocouple to 10 mm. from the base of the crucible only affected the temperature 10° C.

Oil was periodically dropped into the inner crucible by means of a drawn-out glass tube, and the temperature slowly raised until the oil drop burst into flame. If an atmosphere of oxygen be employed a distinct explosion is heard ; in air

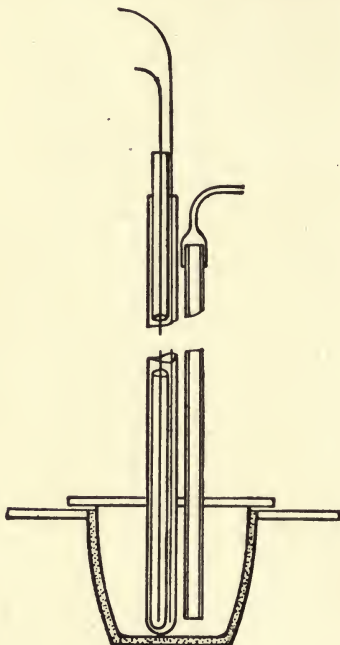


FIG. 40.

only a light puff is audible. The oil at first vaporises a little, and then takes fire. Oils of low asphaltum content and lignite tar oils leave no residue when heated below their ignition point, but asphaltic petroleum oils, coal tar oils, and tars leave cokes. The results obtained by using nickel and platinum crucibles were found to agree closely, but porcelain crucibles yielded higher values. The temperatures were 50° to 100° C. lower when oxygen was employed than with air.

Constam and Schl pfer claim that their results have an experimental error not greater than $\pm 30^{\circ}$ C.

The results of Holm and those of Constam and Schl pfer are in fairly close agreement for such fuels as were examined by both methods, as is shown in the following summary :—

TEMPERATURE OF SPONTANEOUS IGNITION.

	By Holm.	By Constam and Schl�pfer.	
		Platinum Crucible in Oxygen.	Platinum Crucible in Air.
Gas oil - - -	350°	350°	400° to 460° C.
Coal tar oil - -	580°	550°	590° „ 650° C.
Coal tar - - -	500°	480° to 530°	600° „ 630° C.

The author had occasion some time ago to determine several spontaneous ignition temperatures, and as no existing apparatus was sufficiently delicate to differentiate between the samples under examination it was necessary to devise a special instrument for this purpose. This instrument was described in a paper read before the Society of Chemical Industry,¹ from which the following description is extracted :—

“The instrument consists of a diffusion block of 4 in. diameter mild steel bar $3\frac{1}{4}$ in. deep, the base of which has been turned in order to afford a greater heating surface. The upper end of the bar has been machined so as exactly to fit the platinum crucible used for the estimation of the coking values of oils (dimensions, upper diameter 35 mm., diameter of base 22 mm., height 37 mm.).

“A screwed-on cover protects the upper end of the crucible from draughts. This cover is provided with two holes, one for oxygen or air inlet, and one for oil inlet. The oxygen or air is preheated to the temperature of the experiment by passing through a thin copper coil situated in a chamber inside the block.

“A thermometer and a thermocouple pyrometer are fitted into the diffusion block as close as possible to the base of the platinum crucible, and serve to show the temperature of the experiment.

¹ *Journ. Soc. Chem. Ind.*, 15th February 1917, p. 109.

"The method of operation when determining values in oxygen is to heat the block to a given temperature, then pass oxygen through the apparatus at a speed of three bubbles per second. The quantity of oxygen is observed by means of a wash bottle filled with sulphuric acid, which also serves to dry the gas. When the temperature of the block is constant at a desired temperature, one drop of the fuel under examination is allowed to fall through the hole in the centre of the cover of the instrument. If the temperature is much higher than the ignition point a sharp explosion will occur almost immediately, if below the ignition point no explosion takes place. When only slightly above the temperature of ignition the explosion follows some 10 to 12 secs. after the introduction of the oil.

"By repeating the experiments the lowest temperature at which ignition takes place is rapidly determined. This temperature is the temperature of spontaneous ignition. The results obtained by different experimenters using the same instrument agree to within 3° C.

"A similar procedure, using air instead of oxygen, will give the ignition temperature in air, but in this case the explosion is much less violent, and always follows one second after the introduction of the oil."

The construction of the original instrument is clearly seen from the accompanying drawing (Fig. 41). The arrangement of the instrument, with gas burner, thermocouple pyrometer, thermometer, oxygen container, and wash bottle, and screen to protect the instrument from draughts, are shown in the accompanying illustration (Fig. 42).

An improved type of this instrument is now marketed, the difference between this and the original form consisting in a reduction of the size of the crucible, as some trouble was experienced owing to the violence of the explosion in the larger sized crucible, and in the thermometer pocket being deepened by drilling the hole obliquely past the side of the crucible, and the deepening of the radiating fins to facilitate heating. Fig. 42A shows the improved form of instrument.

The author considers that it would be advisable for the

future to adopt oxygen ignition temperatures as standard, as the results are more reliable, and the determinations are cleaner and more convenient.

The influence of the temperature of spontaneous ignition upon the action of a liquid fuel when used in an engine may be considered under two headings.¹ Firstly, in engines where

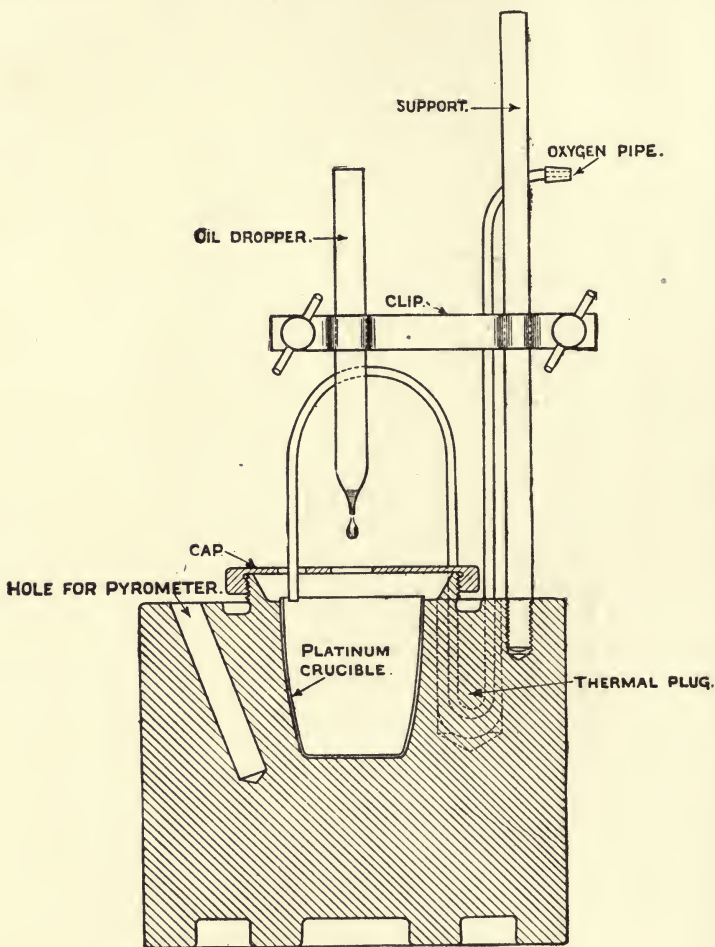


FIG. 42A.

the fuel enters the cylinder before the compression stroke, the temperature of spontaneous ignition indicates the danger of pre-ignition (*i.e.*, of the mixture igniting before the correct time

¹ H. Moore, *The Engineer*, 1917, p. 561.

of firing). Fuels with high ignition points do not pre-ignite so readily, and may be employed in engines with higher com-



APPARATUS FOR TESTING
IGNITION POINT.

FIG. 41.

pressions than fuels of lower ignition point. Secondly, in engines which depend upon the spontaneous ignition of the

fuel as a means of obtaining combustion (*e.g.*, Diesel engines and some semi-Diesel engines), it is necessary to attain such a temperature in the cylinder by the compression that the oil will ignite regularly and immediately.

For the first class of engine it is desirable that a fuel should have a high ignition point, in order that a high compression may be employed, as high compressions are accompanied by high thermal efficiency. With the latter type of engine it is desirable that the fuel should have a low temperature of

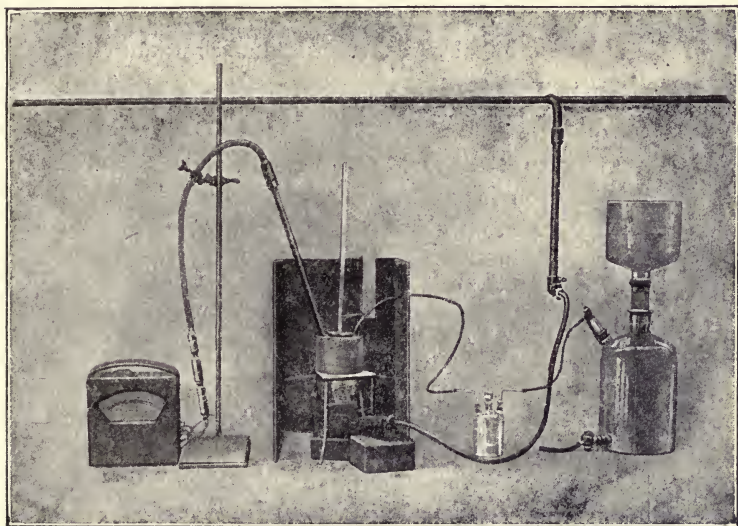


FIG. 42.

spontaneous ignition to ensure regular firing. There is no danger of pre-ignition, as the fuel is not introduced into the cylinder until the end of the compression stroke.

Though the compression attainable in an engine is closely related to the spontaneous ignition point, it is not possible directly to calculate one from the other. All spontaneous ignition tests of liquid fuels determined hitherto, to the author's knowledge, have been made at atmospheric pressure in either air or oxygen, and are therefore not directly applicable to higher pressures. It is, however, possible to

find certain constants which will enable one to determine from the ignition points suitable compressions for any particular type of engine and oil, provided that sufficient data of fuel tests on this type of engine are available.

The temperature obtained by compressing air under conditions such that no escape of heat takes place can be determined by the formula :—

$$T_2 = T_1 \left(\frac{P_2}{P_1} \right)^{\frac{n-1}{n}}$$

where $n = 1.408$,

T_1 and T_2 are initial and final absolute temperatures respectively,

P_1 and P_2 are the initial and final absolute pressures.

The temperature attained in the cylinder of an engine during compression is controlled by the same formula, but it is necessary to modify the value of n in order to allow for leakage and the cooling action of the cylinder walls. The exponent n is not constant for the entire cycle, but the average value for water-cooled internal combustion engines generally lies between 1.30 and 1.38. The value may vary considerably, and when an engine is overheated may exceed 1.408, owing to the absorption of heat from the cylinder walls during compression.

In the accompanying diagram and table (Fig. 43) are shown two curves, one representing the adiabatic compression of a perfect gas from 15° C. (288° absolute), and the other showing the temperatures attained in an engine where $n = 1.35$ and the inlet air has a temperature of 311° absolute (100° F. or 38° C.).

The author has recently extended the use of ignition temperatures by constructing a curve showing the minimum compression practicable on a Diesel engine in order to secure spontaneous ignition with a fuel of any given ignition point, and also a curve showing the maximum compression practicable on a petrol engine in order to avoid pre-ignition with a fuel of any given ignition point. These two curves,¹ together with the average compression-temperature curve

¹ Moore, *The Engineer*, 1917, p. 561.

of internal combustion engines, are shown in the accompanying illustration (Fig. 44).

Ratio in cycles	Total Area	Area under curve	Area above curve
1.	288	15	32
2.	352	79.1	103
3.	395	123	133
4.	430	157	162
5.	459	186	186
6.	485	212	207
8.	526	253	242
10.	561	288	271
12.	589	316	295
14.	619	346	336
16.	649	371	369
20.	705	432	432
25.	739	466	466
30.	765	513	498
40.	840	567	487

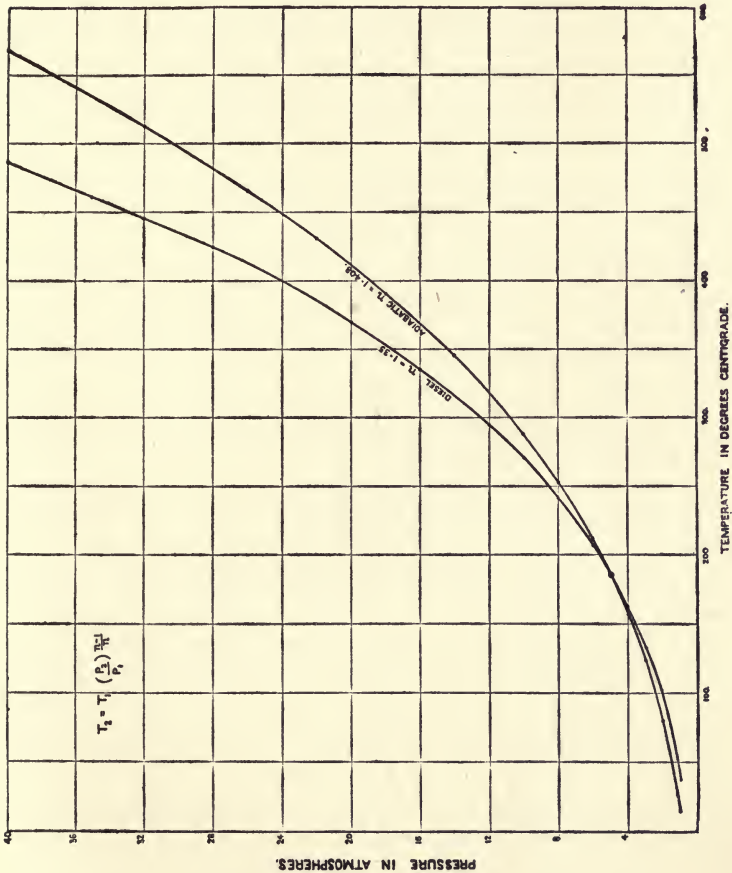


FIG. 43.

As the theoretical and practical efficiencies of engines operating on both the constant volume cycle and the constant

pressure cycle are influenced by the engine compression pressure (see Fig. 45), the dependence of the compression pressure of the engine upon the ignition temperature of the fuel makes the ignition point test one of the most important in the analysis of liquid fuels.

Specific Heat.—It is unnecessary to determine this value, as for oils of any fixed type the variation in specific heat is very slight. The specific heat is required in calculations connected with the heating of fuel tanks and fuel supply pipes.

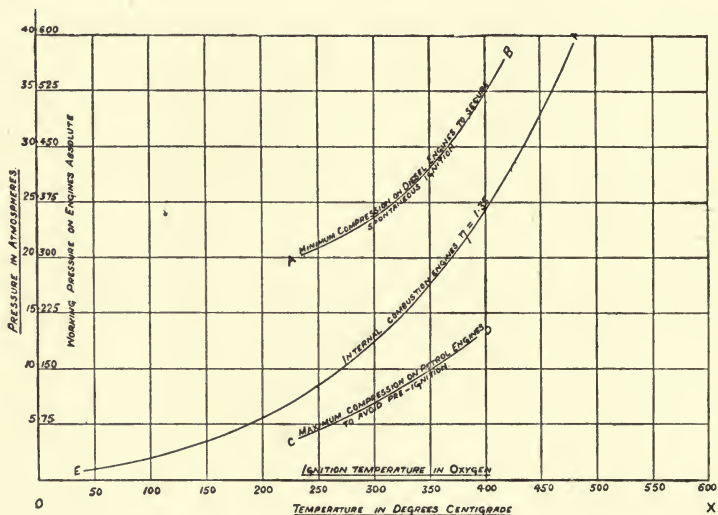


FIG. 44.

The specific heat is the amount of heat required to raise 1 gm. of the substance 1 degree. It is generally stated in terms of water. 1 gm. of water requires 1 calorie to raise its temperature 1 degree centigrade.

The specific heat of the heavier fractions of petroleum have been obtained by Karavayeff,¹ by means of an ice calorimeter. He observed that the mean specific heat of the fractions examined increased rapidly with the temperature. The specific heat of most of the fractions was approximately

¹ Karavayeff, *Neftyanoye Dyelo*, 1913, No. 16; "Petroleum," 1914, p. 550.

0.48 at 100° C., but increased to about 0.60 at 400° C. The specific heat of petroleum fractions of different specific gravity differed but slightly at the same temperatures. Karavayeff states that the true specific heat can be calculated by means of the formula:—

$$\frac{dQ}{dt} = 0.4825 + 0.00077 (t - 100).$$

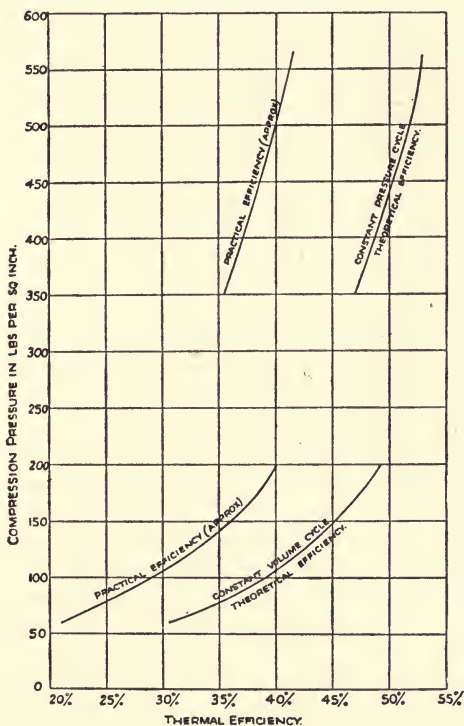


FIG. 45.

Particulars of apparatus and methods of determination of specific heat are given by Graefe,¹ for which purpose he employed a bomb calorimeter. By burning a substance of known calorific power, and filling the container with the oil under examination instead of water, the specific heat of the oil can be calculated from the rise in temperature of the system.

¹ Graefe, "Petroleum," 1907, ii., p. 521.

Kohlrausch¹ has determined the specific heats of liquid fuels by heating the liquid with an electric resistance, the quantity of oil, equivalent of the container, and current used being all known, and the increase in temperature being observed.

SPECIFIC HEAT OF PETROLEUM AND ITS PRODUCTS (KOHLLRAUSCH).

			Temperature of Observation.	Specific Heat.
Petroleum ether	-	-	- 190° C.	0.4518
"	-	-	- 100° C.	0.4446
"	-	-	0° C.	0.4194
Illuminating oil	-	-	21.58° C.	0.511
"	-	-	18.99° C.	0.498
CRUDE PETROLEUM.				
Origin.			Specific Gravity.	Specific Heat.
Japan	-	-	0.862	0.453
Pennsylvania	-	-	0.810	0.500
Russia	-	-	0.908	0.435
California	-	-	0.960	0.398

The specific heat of benzene at from 19° C. to 46° C. is 0.450 cal. (Kopp). Alcohol possesses a specific heat of 0.612 cal.

Vapour Pressure.—The test of vapour pressure is seldom undertaken as a part of a fuel analysis, on account of the length of time taken in making the experiment, and the extreme care necessary in order to obtain accurate results. For the scientific determination of the vapour pressure² an inverted tube, 1 m. long and 10 mm. in diameter, is employed (Fig. 46). This tube is sealed at the upper end, and contains a mercury column. The length of tube is sufficient to form a Torricellian vacuum at the upper end, whilst the bottom end is immersed in a dish full of mercury. The tube (which is a complete barometer) is surrounded by a glass jacket by means of which water can be circulated round the tube in order to maintain any desired temperature. An excess of the substance under examination is passed into the tube by

¹ Kohlrausch, "Lehrbuch der Practischen Physik," 1910, p. 197.

² Kohlrausch, "Practische Physik."

means of a pipette with a bent nozzle. The vapour pressure is found by measuring the height of the mercury column before and after the addition of the substance.¹

Sir Boverton Redwood and Captain Thomson have devised an apparatus, by means of which comparative tests can be made of the vapour pressures of motor spirits. This apparatus is described by V. B. Lewes² as follows:—

“The apparatus consists of a thick-walled glass tube of small bore, about 30 in. long. The lower end of the tube is turned up and widens into a cylinder, about 6 in. long and 1 in. diameter, the upper end of which terminates in a short length of glass tube. The long tube is graduated in inches, divided into tenths, and the wide cylinder is provided with two marks, the lower corresponding with the zero of the scale, and the upper being placed at nine-tenths of the capacity of the cylinder above the lower mark. In use a short length of stout rubber tubing is wired to the tube at the top of the cylinder, so as to cover it entirely, and project about $\frac{3}{4}$ in. above it. Mercury is poured into the cylinder up to the lower mark, and care is taken that the mercury thread in the capillary tube is not broken. Enough of the liquid under test is poured into the cylinder to fill it well up to the upper mark, and the apparatus is clamped vertically in a vessel of water at 50° F. After sufficient time has elapsed to allow of this temperature being attained by the apparatus and its contents, the level of the liquid is corrected, if necessary, and the rubber tubing is closed by a pinch cock screwed up very firmly just above the top of the glass tube, the open end of the india-rubber tube being further closed by a glass stopper.



FIG. 46.—Apparatus for Determining Vapour Pressure.

¹ Particulars of a new instrument for the determination of vapour tensions, by the author, are given in *The Automobile Engineer*, September to October 1919.

² Professor V. B. Lewes, “Motor Fuels,” Fothergill Lectures, Roy. Soc. of Arts, 1915.

The whole apparatus is immersed above the top of the rubber tube in water at 50° F. The temperature of the water is raised very slowly by means of a rose burner, and its temperature read by means of a thermometer immersed in it, unequal heating being avoided, as far as possible, by any form of mechanical stirrer. As the temperature of the water rises the height of the column of mercury in the capillary tube is read off at every 5° F. rise of temperature in the liquid, the heat being so regulated that this rise takes about ten minutes, and is continued to 100° F."

The vapour pressure is mainly of interest in connection with the examination of motor spirits. The ease of starting a petrol engine is dependent upon the vapour pressure of the fuel. Danger from fire and pressure on sealed storage tanks containing motor spirits are also dependent upon vapour pressure.

Vapour Density.—This is a test very rarely required in connection with motor fuels, the approximate density being generally roughly obtainable from a knowledge of the chemistry of the fuel in question. If it is necessary to make a determination, the methods used for molecular weight determination may be employed. Particulars of these may be found in any book on physical chemistry.

Latent Heat of Vaporisation.—When a substance changes its physical state from solid to liquid, or from liquid to gaseous, a certain amount of heat is absorbed. When the change is from the liquid to the gaseous state, this quantity of heat is known as the latent heat of vaporisation. This value is mainly of interest in connection with the design of carburetters and vaporisers, where the cooling of the vaporising space is dependent upon the latent heat of vaporisation. The phenomenon of cooling is frequently exhibited on automobile carburetters, where it is not unusual to find snow formed on the sides of the carburetter by the low temperature caused by the vaporisation of the fuel.

It is not usual to determine the latent heat of vaporisation of oils,¹ but this value can be closely estimated from that of the pure hydrocarbons which they are known to contain.

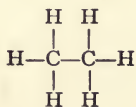
¹ Holde, "Untersuchung der Kohlenwasserstofföle u. Fette," p. 18, gives particulars of the apparatus and method for determining the latent heat of vaporisation.

LATENT HEAT OF VAPORISATION.

ALIPHATIC HYDROCARBONS.			
Substance.	Formula.	Boiling Point.	Latent Heat in Calories.
Hexane - - - -	C_6H_{14}	69° C.	79·4
Heptane - - - -	C_7H_{16}	98° C.	74·0
Octane - - - -	C_8H_{18}	125° C.	71·1
HYDRO-AROMATIC HYDROCARBONS.			
Hexamethylene - -	C_6H_{12}	80° C.	87·3
Dimethylpentamethylene -	C_7H_{14}	90°-92° C.	81·0
Methylhexamethylene -	C_7H_{14}	98° C.	75·7
Dimethylhexamethylene -	C_8H_{16}	118°-119° C.	71·7
BENZENE AND ALCOHOL.			
Benzene - - - -	C_6H_6	80·4° C.	94·4
Ethyl alcohol - - -	C_2H_5OH	78·5° C.	203·0

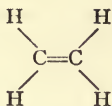
Iodine and Bromine Tests.—Organic compounds which contain carbon atoms held together by more than one bond are unstable to many chemical reagents. When compounds contain atoms connected by more than one bond they are known as unsaturated compounds. Bromine and iodine, being chemically very active, are absorbed by unsaturated compounds to form bromides and iodides. Take for example the two hydrocarbons ethane and ethylene.

Ethane, formula—



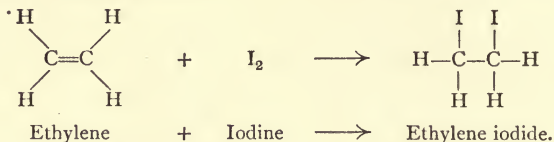
—is a saturated hydrocarbon, and does not absorb iodine or bromine.

Ethylene, formula—



—is an unsaturated hydrocarbon, and will absorb iodine or bromine.

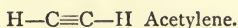
When iodine comes into contact with ethylene the following reaction takes place:—



Oils always contain some unsaturated hydrocarbons, and a measure of the amount of these present may be obtained by an estimation of the quantity of iodine or bromine which they will absorb.

By treating an oil with a measured excess of a suitable solution of iodine, and then estimating the unabsorbed iodine, it can be accurately determined how much iodine has combined with the oil. The value thus obtained is known as the iodine value, and is stated in milligrams of iodine per gram of oil. The iodine value, therefore, represents the degree of unsaturation, or the proportion of double bonds present in an oil.

Unsaturated hydrocarbons possess a greater proportion of carbon than the corresponding saturated hydrocarbons, and this, together with their comparative instability, makes them more liable to precipitate carbon during combustion than similar saturated hydrocarbons. As an example of this take the three gases, ethane (C_2H_6), ethylene (C_2H_4), and acetylene (C_2H_2), the first of which is saturated, while the second contains a double bond, and the third contains a triple bond—



Ethane burns with an almost non-luminous flame, while the flame of ethylene is highly luminous, and acetylene will deposit carbon unless burned with a special burner.

Similarly it will be found that fuels of high iodine value are more liable to precipitate carbon in the cylinders of internal combustion engines than fuels of low iodine value.

The tendency towards carbonisation of fuel oils is, however, more clearly exhibited by the proportion of carbon to hydrogen found in the elementary analysis, a proportion which has also been used to show the difficulty of obtaining ignition if the oil is required for use in a Diesel engine.¹

The iodine value is of more importance in connection with compressor lubrication² and transformer oil³, where it is an indication of the liability to oxidation. Radcliffe and Polychronis⁴ have investigated the methods of determining the iodine values of mineral oils. They recommend the use of Wij's solution, and the following procedure:—

"To prepare Wij's solution glacial acetic acid was fractionally distilled, and the portion boiling at 118·5° C. collected for the preparation of the reagent. The acid used did not reduce chromic acid. Exactly 8·5 gm. of pure resublimed iodine was added to about 400 c.c. of the acetic acid contained in a dry flask fitted with a calcium chloride tube to exclude moisture, and to another 400 c.c. of the acid contained in a similar flask was added 7·8 gm. of pure iodine trichloride. The two flasks were gently warmed and shaken until everything was dissolved, then cooled, the contents mixed, and made up to one litre with the acetic acid used for rinsing the flask."

0·2 to 0·3 gm. of oil was taken in each case in a 500 c.c. stoppered bottle, 10 c.c. of carbon tetrachloride added, and, when the oil had dissolved, 25 c.c. of the reagent were run in from a pipette. Blank tests should be conducted in each case. After standing in a dark place for twenty-four hours, 20 c.c. of a 10 per cent. potassium iodide solution were added, and finally 300 c.c. of cold water, and the excess iodine titrated with decinormal sodium thiosulphate solution, starch being used as indicator. The iodine absorbed is calculated from the difference between the values obtained from the blank test and the tests in which oil is used. The results are stated in milligrams of iodine per gram of oil.

¹ Rieppel, *Zeits. Ver. d. Ing.*, 1907, No. 16, p. 613.

² Moore, *The Engineer*, 20th August 1915.

³ Pollard Digby, *Journ. Inst. Elect. Eng.*, vol. liii., No. 239, p. 146.

⁴ *Journ. Soc. Chem. Ind.*, 31st March 1916.

CHAPTER XII

CALORIMETRY

AS the work obtainable from any fuel is dependent on the amount of heat given by its combustion, the determination of the quantity of heat yielded by a unit weight of fuel is of fundamental importance. The measure of heat given by the combustion of a fuel is called the calorific power, or calorific value. This is an entirely different value from the calorific intensity, which is the maximum temperature obtainable by the combustion of a fuel.

The quantity of heat is measured by two units, the calorie and the British Thermal Unit. The calorie is the amount of heat required to raise one gram of water one degree centigrade (though this quantity varies slightly at different temperatures, no standard temperature has been adopted). Callendar determined the specific heat of water between 0° C. and 100° C. The specific heat (taken on a basis of 1.000 at 20° C.) was found to exceed 1.010 at 0° C., to fall to a minimum at 40° C., and to rise to 1.007 at 100° C. The Calorie (spelt with capital C) is one thousand calories. The British Thermal Unit (abbreviated to B.Th.U.) is the amount of heat required to raise one pound of water from 60° F. to 61° F. When measuring the heat given by burning a fuel, either the number of calories given by the combustion of one gram of fuel or the number of B.Th.U. given by the combustion of one pound of fuel is employed.

One kilogram is roughly 2.2 lbs., and one degree centigrade is $\frac{9}{5}$ ths of one degree F., therefore one Calorie is $\frac{9}{5} \times 2.2 = 3.96$ B.Th.U. One calorie is .003968 B.Th.U. One B.Th.U. is 0.252 Calorie, or 252 calories.

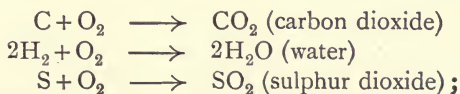
When the calorific power of a fuel is stated in calories it is assumed that one gram of fuel has been taken, whereas when the value is stated in B.Th.U. it is understood that the heat is evolved by one pound of fuel; the relationship,

therefore, between calories and B.Th.U., *when stating the calorific power of a fuel*, is the relationship between the Fahrenheit and the centigrade degrees. Suppose that an oil has a calorific value of 10,000 cal., this means that the combustion of one gram of oil will raise the temperature of 10,000 gm. of water one degree centigrade. It is evident that the combustion of one pound of this oil would raise 10,000 lbs. of water one degree centigrade, and as one degree centigrade is 1.8° F., the heat yielded would be $1.8 \times 10,000 = 18,000$ B.Th.U., or $\frac{5}{9}$ ths the number of the calories. From this it will be seen that *when referring to the calorific power of a fuel*.—

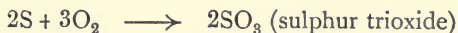
$$\begin{aligned} 1 \text{ calorie} &= 1.8 \text{ B.Th.U.} \\ \text{and } 1 \text{ B.Th.U.} &= \frac{5}{9} \text{ calorie.} \end{aligned}$$

The calorific power of a fuel may be determined either by calculation from the ultimate analysis of the fuel, or by experiment, *i.e.*, by using a calorimeter.

The Calculation of Calorific Power.—The only elements found in appreciable quantities in fuels are carbon, hydrogen, sulphur, oxygen, and nitrogen. Fuels yielding an ash contain traces of other elements, which it may be assumed will not affect the heat value of the fuel. These elements when burned undergo chemical changes. The final products, if the combustion be complete, may be seen from the following equations :—



and sometimes :—



The oxygen and nitrogen may be considered as leaving the combustion space without combining.

When these chemical changes take place heat is evolved in the following amounts :—

1 gm. carbon burns to carbon dioxide with the evolution of 8,137 cal.

1 gm. hydrogen burns to form water (in the liquid form), yielding 34,500 cal.

1 gm. sulphur burns to form sulphur dioxide, yielding 2,200 cal.

1 gm. sulphur burns to form sulphur trioxide, yielding 3,300 cal.

As sulphur generally burns with the formation of both sulphur dioxide and sulphur trioxide, it is common to consider the calorific power of sulphur as 2,500 cal. If only carbon, hydrogen, and sulphur were present, assuming oils to be composed of the elements in a state of mixture, we should therefore obtain the formula :—

$$\text{Calorific power} = \frac{(C \times 8137) + (H \times 34500) + (S \times 2500)}{100},$$

where C, H, and S are the percentages of carbon, hydrogen, and sulphur respectively present in the fuel. Now when oxygen is present it is found that the heat value is lowered, and it is most satisfactory to assume that the oxygen is present in combination with the hydrogen (as water). Hydrogen combines with eight times its weight of oxygen to form water, therefore one-eighth of the oxygen content of the fuel must be deducted from the hydrogen content before the heat value is calculated. This leaves the formula :—

$$\text{Calorific power} = \frac{8137 C + \left(H - \frac{O}{8}\right) 34500 + 2500 S}{100}.$$

In an internal combustion engine the water leaves the engine in the form of steam, whereas the above formula is based on the assumption that the water is condensed. A deduction must therefore be made from the above formula as an allowance for the latent heat taken away by the water formed during the reaction. The lower heat value obtained after this deduction is known as the net calorific power. The latent heat amounts to approximately 600 cal. per gram of water, or 54 cal. for each per cent. of hydrogen present in the original fuel.

Net Calorific Power = Gross Calorific Power — 54 H.

The hydrogen content of light petroleum products (petrol) is about 14 per cent., therefore there is $54 \times 14 = 756$ cal. difference between the gross and the net calorific powers.

Similarly, with heavy petroleum oil there is about 658 cal., but with tar oils only about 324 cal. difference between the gross and net calorific powers.

The foregoing formulæ make no allowance for the heat changes which have taken place in the formation of the compounds present in the fuel from their elements, and on this account the calculated calorific powers are never very reliable. The errors introduced in the combustion process (the ultimate analysis) are considerable, and are multiplied in the calculation of calorific power. The experimental determination of calorific values is more rapid, easier, and more accurate than the process of obtaining them from the ultimate analysis. For technical purposes it is not generally necessary to make an ultimate analysis, therefore the direct determination by means of a calorimeter is in all respects preferable. Calculations of calorific value are seldom made where a good calorimeter is available, but are frequently made to serve in laboratories which possess no calorimeter.

Experimental Determination of Calorific Value.—

The experimental determination of calorific power is made by means of a calorimeter, an instrument in which a small quantity of the fuel is burned, the heat evolved being measured. The relative estimation of the heat value of boiler fuels by actual trial need not be treated here. Calorimeters may be divided into three classes, depending upon the means which are employed for supplying to the fuel the oxygen necessary for combustion:—

(1) Calorimeters employing oxygen at approximately atmospheric pressure.

(2) Calorimeters in which a solid oxidising agent is employed (*e.g.*, sodium peroxide).

(3) Calorimeters in which the combustion takes place in high pressure oxygen (bomb calorimeter).

Gas calorimeters are not included in the above classes. Of these three classes only the bomb calorimeters are suitable for use with liquid fuels. The original bomb calorimeter was devised by Berthelot, and has since undergone many modifications. There are several calorimeters at present on the market, and as the majority of these instruments only differ in detail, it will not be necessary to describe more than

one example, the Cook-Mahler bomb, which the author uses for liquid fuel determinations. For more detailed information on the subject treatises on calorimetry should be consulted.¹

The bomb calorimeter consists of a steel vessel, capable of withstanding 200 atmospheres pressure, lined either with platinum (which is the most satisfactory but most expensive lining) or with enamel. The vessel is provided with a cover, so attached as to make a perfectly tight joint when in use. The cover contains one or two passages leading to the inside of the bomb, each controlled by conical seated valves. An insulated electric terminal passes through the cover, and is so constructed as to withstand high pressures without leakage. This terminal conducts an electric current which serves to fuse a thin wire inside the bomb, this being the means employed for igniting the oil. The body of the bomb acts as the other electric connection. This vessel is enclosed in a light metal vessel of some three litres capacity, which during the experiment contains a measured quantity of water. It is polished on the outer side to minimise radiation. The water container rests on insulating supports (*e.g.*, corks), and is separated from the outer jacket by an air space. The outer jacket is either made of insulating material, or, better, is a metal jacket filled with water and covered with insulating material on the outer side. The upper portion of the apparatus is provided with a cover through which passes a stirring gear, used to agitate the water in the container during experiments. Through this cover are passed the electric wires and a Beckmann thermometer. In the accompanying diagram (Fig. 47) is shown a section of the Cook-Mahler bomb. Fig. 48 shows section of container and jacket with bomb in position.

In the calculation of the results of a calorimeter determination it is necessary to know the water equivalent of the instrument. This value has to be obtained either by weighing those parts of the instrument which change temperature during the determination, and calculating their water equivalent from the specific heats of the metals of which

¹ "Examination and Thermal Value of Fuels, Gaseous, Liquid, and Solid," by Coste and Andrews.

these parts are made, or by a special determination, in which a pure chemical compound of known calorific power is used.

When a sample of fuel is burned in the calorimeter the heat evolved is diffused through the bomb body, surrounding water, water container,

stirring gear, and thermometer.

The rise in temperature is noted,

and as the quantity of water in the container

has been measured, the number of calories

which have been taken into this water is obtained

by multiplying the rise in temperature

by the weight of water present. The parts of

the instrument which are in contact with this

water will undergo an equal rise in temperature,

so it is necessary to know how many calories

are taken up by these parts in order to raise their

temperature 1° C. This value

is called the water equivalent of the calorimeter.

The calorimeter equivalent can be experimentally

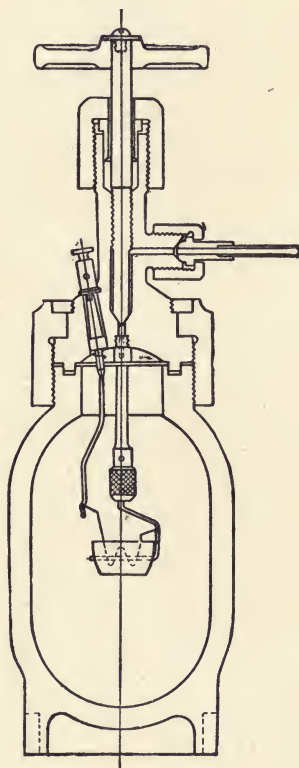
found by proceeding exactly as if a calorific

power were being estimated, but burning a

substance of known value. As a known quantity of

heat has been generated from the substance burned, the

equivalent of the instrument is found by dividing the rise



SECTION THRO' BOMB OF COOK-MAHLER
BOMB CALORIMETER

FIG. 47.

As a known quantity of heat has been generated from the substance burned, the equivalent of the instrument is found by dividing the rise

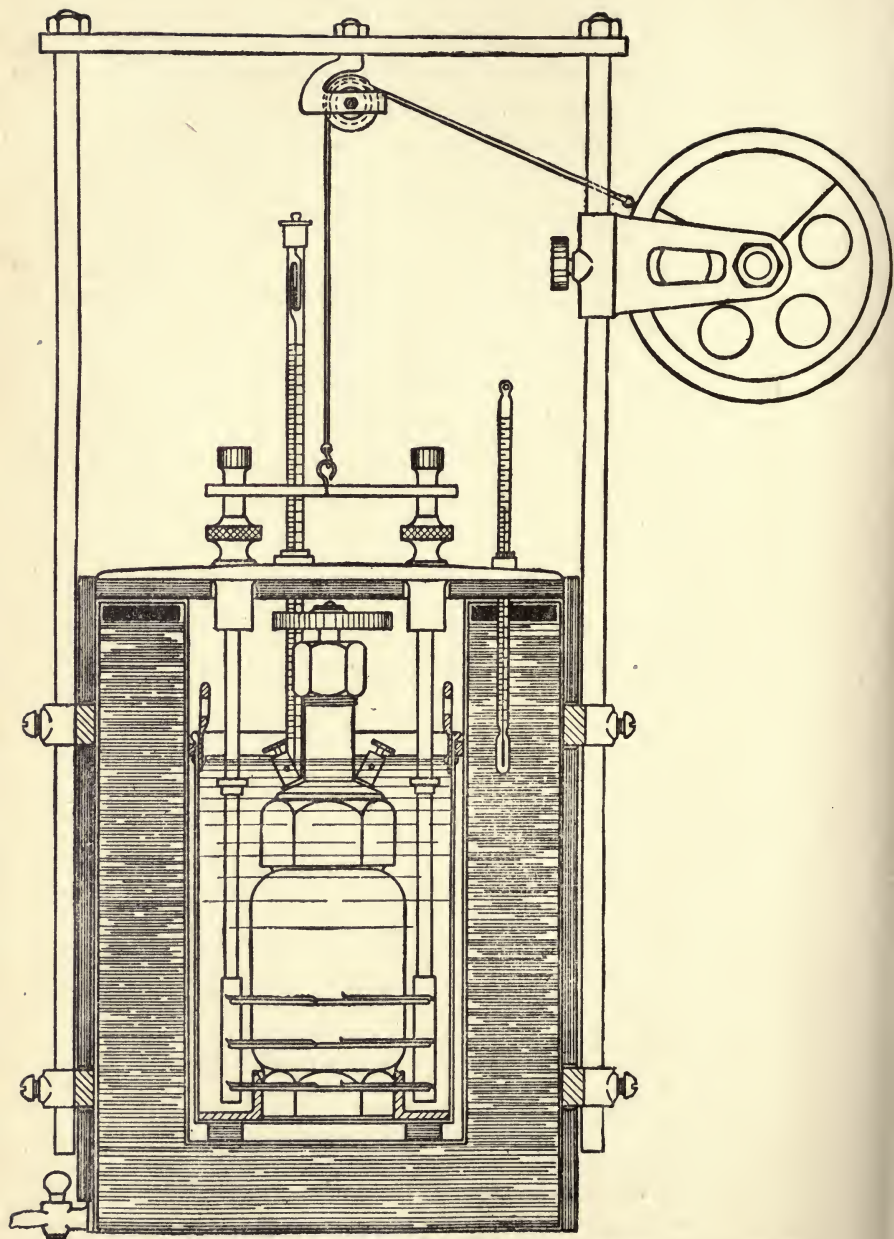


FIG. 48.—Section through Jacket and Container of Cook-Mahler Bomb, showing Bomb and Stirring Gear in Position.

in temperature into the heat generated (which gives the equivalent of the instrument, together with water in container), and then subtracting the number of grams of water used in the container.

The substances generally employed for the standardisation of bomb calorimeters are :—

Naphthalene	.	-	-	-	9,688 cal.
Benzoic acid	-	-	-	-	6,325 „
Cane sugar	-	-	-	-	3,955 „

Coste and Andrews recommend the use of cellulose (4,209 cal.).¹ Naphthalene and benzoic acid require to be melted into a No. 000 crucible for the determination ; if not melted, the fine crystals are blown out of the crucible and deposited on the bomb walls.

The calorific value of a heavy oil is determined in a bomb calorimeter in the following manner. The platinum fuse wire, .0025 in. thick, is connected as shown in Fig. 47. Approximately 1 gm. of the sample is weighed out into the fuel crucible, and the crucible placed in position with fuse wire partly immersed in the oil. The bomb cover is then quickly screwed into position. The joint between the cover and the body of the bomb is generally made with lead wire, and is easily replaced in case of wear. It should be examined before an estimation is made, and, if necessary, replaced. The bomb is then connected to the oxygen cylinder, and a pressure gauge placed in the circuit so as to read the bomb pressure. Oxygen is now allowed to flow into the bomb until a pressure of 25 atmospheres is registered on the pressure gauge. All valves are now closed down, and the bomb disconnected. The container is filled with a measured quantity of water (this quantity depends upon the type of calorimeter employed). With the Cook calorimeter the author employs 2,500 gm. of water. The temperature of the water should be approximately that of the room, or slightly below room temperature. The bomb is now connected to the electric wires, a suitable resistance and switch being in series. The bomb is immersed in the water of the container. The container, stirring gear, and cover are placed in position.

¹ Coste and Andrews, "Examination and Thermal Values of Fuels, Solid, Liquid, and Gaseous," p. 265.

After the entire instrument has been standing some ten minutes, to allow equalisation of temperature, the stirring gear is set in motion and temperature readings taken every half minute. Beckmann thermometers are the most suitable type of mercurial thermometer for calorimetry, and for industrial purposes they should be graduated to $\frac{1}{100}^{\circ}$ C. The third decimal place of the temperature reading can be estimated by the eye, or better, by means of a small pocket lens. When the temperature of the instrument is constant, or the change in temperature has become regular, the electric current is switched on for an instant. The stirring gear is worked regularly through the entire experiment. The temperature is noted until the difference in temperature between each reading becomes regular. A graph of a set of readings of calorimeter temperatures against time is shown in Fig. 49. By subtracting the initial temperature from the maximum the increase in temperature is obtainable. The calories yielded by the combustion of the oil will therefore be obtainable by the formula:—

$$c = (W + w)t,$$

where W is the number of grams of water in the container, w is the water equivalent of the instrument, and t is the rise in temperature, provided that no leakage or absorption of heat has taken place between the calorimeter and its surroundings during the experiment. If thermal equilibrium be obtained between the calorimeter and its surroundings at the commencement of an experiment the conditions will be altered when the container has risen in temperature. Some experimenters have overcome these errors by arranging to heat the surrounding jacket at the same rate as the container. Such a proceeding is not convenient or necessary for industrial purposes, but as the errors introduced by leakage of heat are considerable, it is necessary to make a correction for these in the calculation of the results of the experiment. If the temperature of the jacket can be so arranged that it is the mean temperature of the container before and after the experiment the leakage is much reduced, but this system is not theoretically correct unless the increase in the temperature of the container is regular, which is not usual.

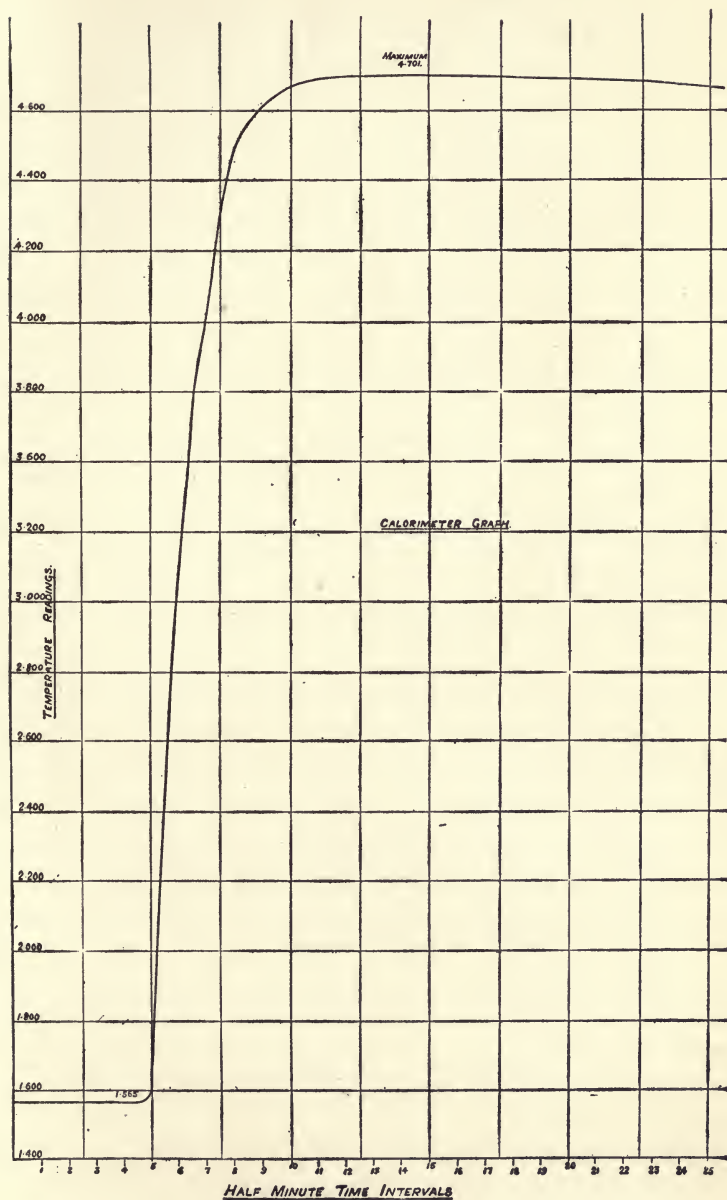


FIG. 49.

In the experiment shown in graph (Fig. 49), the temperatures recorded were as follows:—

	Interval (30 Seconds Each).	Average Temperature of Interval.	Main Increase from Initial Temperature.
1	1·565
2	1·565
3	1·565
4	1·565	1·58	·02
5	1·600		
6	3·02		
7	4·01		
8	4·49	4·25	2·69
9	4·61	4·55	2·99
10	4·67	4·64	3·08
11	4·69	4·68	3·12
12	4·70	4·69	3·13
13	4·700	4·70	3·14
14	4·701	4·70	3·14
15	4·700	Total of interval differences.	24·02
16	4·699		
17	4·698		
18	4·695		
19	4·693		
20	4·690		
21	4·688		

Loss per interval after experiment $\frac{·010}{4} = ·0025°$.

Loss per interval per degree rise above initial temperature
 $= \frac{·0025}{3·14} = ·0008°$.

Loss due to cooling = $24·02 \times ·0008 = ·0192°$.

Difference between initial and maximum temperature = 3.136° .

Loss due to cooling = $.019^{\circ}$.

Corrected rise in temperature = 3.155° .

Equivalent of bomb	-	-	836 cal.
Weight of water taken	-	-	2,500 gm.
Equivalent of bomb and water	-	-	3,336 cal.

$$\text{Calorific power} = \frac{(W + w)t}{\text{Weight of oil taken}}$$

For this experiment 1.0000 gm. of oil was taken.

$$\text{Therefore calorific power of oil} = \frac{3336 \times 3.155}{1.000}$$

Log. 3,336	-	-	-	-	3.5232
Log. 3.155	-	-	-	-	.4990
Log. product	-	-	-	-	4.0222
Antilog. 4.0222	-	-	-	-	= 10,525
Gross calorific power of oil	-	-	-	-	= 10,525 cal.

A simpler method of calculation of the cooling correction which yields approximate results, though not theoretically correct, is to take the rate of cooling before and after the experiment, and consider that the mean of these values has been the rate of cooling throughout the experiment.

Such a method applied to the above experiment would yield the following figures:—

Rate of cooling before firing oil	-	.0000° per interval.
„ after „	-	.0025° „
Mean rate of cooling	-	.00125°
Number of intervals between firing and maximum	-	10
Cooling correction	-	$10 \times .00125 = .0125^{\circ}$

The cooling correction may be calculated by many more complex and more efficient methods than those stated, but for commercial purposes the method first given will be found sufficiently accurate.

In addition to the foregoing calculation, it is necessary when accuracy of results are required to make allowance for the heat evolved by the burning of sulphur into sulphur trioxide. In normal practice sulphur burns mainly into the dioxide (SO_2), but under the conditions prevailing in the bomb calorimeter the sulphur is burned to the trioxide (SO_3),

with the evolution of more heat than the normal combustion yields. The solution of the trioxide in the water formed by the combustion results in the evolution of a further quantity of heat. The heat liberated by the further combustion of sulphur dioxide into sulphur trioxide, and the solution of the latter product in water, is approximately 2,250 cal. per gram of sulphur. It will therefore be necessary to deduct $22\frac{1}{2}$ cal. from the experimental gross calorific value for each per cent. of sulphur present in the original fuel, in order to obtain values corresponding to normal combustion. A further correction is necessary on account of nitric acid, a product which is formed both from the nitrogen of the air and that contained in the oil during the combustion in a calorimeter. As nitric acid is not a product of normal combustion, it is necessary to make an allowance for the heat liberated during its formation. The combined nitric and sulphuric acid present in the bomb liquor is obtainable by titration with sodium carbonate, using methyl orange as indicator. The sulphuric acid may be determined afterwards by precipitation with barium chloride (see sulphur estimation). The nitric acid content is therefore obtained by deducting the sulphuric acid from the total acidity. The heat of formation of nitric acid is 227 cal. per gram.

As an example of this calculation may be given the following case :—

It was found that 1 gm. of oil burned in calorimeter yielded 0.957 gm. barium sulphate, and required 22.55 c.c. of $\frac{N}{10}$ sodium carbonate to neutralise, using methyl orange as indicator.

0.957 gm. barium sulphate contains $0.957 \times 0.137 = 0.131$ gm. sulphur = 1.31 per cent. sulphur.

$1.31 \times 22\frac{1}{2} = 29.5$ cal. sulphur deduction.

0.957 gm. barium sulphate is equivalent to $\frac{98}{233} \times 0.957$

$= 0.402$ gm. sulphuric acid $= \frac{0.402}{0.0049}$ c.c. $\frac{N}{10}$ sulphuric acid

$= 8.20$ c.c. $\frac{N}{10}$ sulphuric acid,

which is equivalent to 8.20 c.c. $\frac{N}{10}$ sodium carbonate.

But titration of total acidity required 22.55 c.c. $\frac{N}{10}$ sodium carbonate, $\therefore 22.55 - 8.20 = 14.35$ c.c. $\frac{N}{10}$ nitric acid was present.

14.35 c.c. $\frac{N}{10}$ nitric acid $= 14.35 \times .0063 = .0904$ nitric acid,
 \therefore correction for nitric acid $= 227 \times .0904 = 20.5$ cal.

The nitric acid correction is generally about 15 cal., but the sulphur varies considerably, and may reach as much as 80 cal.

APPENDIX

CALORIFIC PROPERTIES OF VARIOUS FUELS.

Substance.	Calorific Power.		Observed by.
	Calories.	B.Th.U.	
Scotch peat briquettes (16% H_2O)	4,754	8,558	F. Mollwo
Coke from Scotch peat -	7,600	13,680	Perkin
Oak (containing 13·3% H_2O)	3,990	7,182	F. Mollwo
„ „ 11·8 „	4,155	7,479	Perkin
Yoke elm (containing 12·2% H_2O)	4,151	7,490	Gottlieb
Beech (containing 12·95 % H_2O)	4,168	7,502	„
Beech (containing 13·95 % H_2O)	4,101	7,382	„
Beech (containing 13·75 % H_2O)	4,114	7,405	„
Birch (containing 11·83 % H_2O)	4,207	7,573	„
Pine (containing 12·17 % H_2O)	4,422	7,960	„
Fir (containing 11·80% H_2O)	4,485	8,073	„
Anthracite - - -	8,400	15,120	Dosch
„ from Westphalia	7,575	13,635	Langbein
Short flame sinter coal -	8,200	14,760	Dosch
Kentucky coal (U.S.A.) -	7,785	14,013	U.S. Geological Survey
Illinois coal „ -	7,056	12,701	U.S. Geological Survey
Pennsylvania coal „ -	7,875	14,175	U.S. Geological Survey
Coke - - - -	6,900	12,420	Dosch
„ - - - -	6,919	12,454	Langbein
Lignite - - - -	4,000	7,200	Dosch
Earthy lignite - - -	3,000	5,400	„
Lignite briquettes - -	4,668	8,402	Langbein
Lignite from Saxony (moist)	2,622	4,720	„
Peat - - - -	4,230	7,614	„
Sawdust briquettes - -	4,065	7,317	„
Asphaltum (extracted from petroleum)	9,550	17,190	H. Moore
Dry peat (average from bog)	4,490 to 6,140	8,100 to 11,000	Anderson and Dillner
„ reed grass peat - -	4,140 to 5,460	7,450 to 9,820	Anderson and Dillner
„ mud peat - - -	4,360 to 4,560	7,825 to 8,200	Anderson and Dillner

THE HEAT OF COMBUSTION OF SEVERAL BODIES WITH OXYGEN OR AIR.

The following determinations were made by Berthelot (B), Favre and Silberman (F), Thomsen (Th), Stohman (St), and Moore (M).

Substance.	Products of Combustion.	Calories K per Kilogram.	Observed by
Wood charcoal - - -	CO ₂	8,080	F
" " - - -	"	8,137	B
Sugar " - - -	"	8,040	F
Retort graphite - - -	"	8,047	"
Blast furnace graphite - - -	"	7,762	"
" " " - - -	"	7,901	B
Natural graphite - - -	"	7,997	F
Carbon monoxide, CO - - -	"	2,403	"
" " " " - - -	"	2,440	B
Wood charcoal - - -	CO	2,473	F
" " " - - -	"	2,442	B
Hydrogen - - -	H ₂ O liquid	34,462	F
" " - - -	"	34,180	Th
" " - - -	H ₂ O steam	28,800	"
" " - - -	"	29,150	B
Methane, CH ₄ - - -	CO ₂ + H ₂ O liquid	13,063	F
" " - - -	"	13,344	B
" " - - -	" steam	12,066	"
Acetylene, C ₂ H ₂ - - -	" liquid	11,927	"
" " - - -	" steam	11,527	Th
Ethylene, C ₂ H ₄ - - -	" liquid	11,858	F
" " - - -	"	12,072	B
" " - - -	" steam	11,293	"
Propylene, C ₃ H ₆ - - -	" liquid	11,934	"
" " - - -	" steam	11,155	"
Benzene, C ₆ H ₆ (gaseous) - - -	" liquid	10,070	"
" " - - -	" steam	9,650	calculated
Naphthalene, C ₁₀ H ₈ - - -	" liquid	9,664	B
" " - - -	" steam	9,328	calculated
Creosote from Paris (10% tar acids) - - -	" liquid	9,253	M
" " " (no tar acids) - - -	"	9,501	"
Tar acids from Paris creosote - - -	"	7,995	"
Paraffin - - -	"	11,140	St
" " - - -	" steam	10,340	"
Hexane, C ₆ H ₁₄ - - -	" liquid	11,525	"
" " - - -	" steam	10,636	"
Heptane, C ₇ H ₁₆ - - -	" liquid	11,375	F
Alcohol, C ₂ H ₆ O - - -	"	7,184	F
" " - - -	"	7,054	B
Glycerin, C ₃ H ₈ O ₃ - - -	"	4,316	St
Starch, C ₆ H ₁₀ O ₅ - - -	"	4,228	B
Cellulose, C ₆ H ₁₀ O ₅ - - -	"	4,208	"
Dextrose, C ₆ H ₁₂ O ₆ - - -	"	3,762	"
Cane sugar, C ₆ H ₂₂ O ₁₁ - - -	"	3,963	"
Stearic acid - - -	"	9,374	St
Rhombic sulphur - - -	SO ₂	2,221	F
" " - - -	"	2,166	B
Monoclinic sulphur - - -	"	2,241	Th
Carbon disulphide - - -	CO ₂ + SO ₂	3,333	B
Silicon - - -	SiO ₂	7,407	"
Copper - - -	CuO	590	Th

ANALYSIS OF COALS (GRAY AND ROBINSON).

	1	2	3	4	5	6	7	8	9	10	11	12
Carbon	-	62.55	68.64	69.50	72.14	73.77	74.99	74.57	77.00	76.71	78.80	85.70
Hydrogen	-	3.87	4.33	4.42	4.40	4.55	4.66	4.74	4.51	4.67	4.92	2.97
Sulphur	-	1.62	1.33	0.67	0.61	0.41	0.55	0.47	0.78	0.73	0.50	0.62
Water	-	8.63	8.96	9.28	8.34	7.99	7.21	6.95	2.31	1.94	2.72	3.15
Ash	-	11.78	6.90	5.97	4.22	1.76	2.68	1.37	7.17	8.49	4.18	3.59
Oxygen and nitrogen	-	11.55	9.84	10.16	10.29	11.52	9.91	11.90	8.23	7.46	8.88	3.90
Coke	-	61.74	57.53	59.12	58.47	56.93	56.59	56.84	74.61	72.32	66.43	92.03
Fixed carbon	-	49.96	50.03	53.15	54.25	55.17	53.91	55.47	67.44	63.83	62.25	88.44

- | | |
|---|--|
| 1. Splint coal, Lochgelly, Fife. | 7. Splint coal, Bothwell. |
| 2. Boiler fuel (a mixture), Fife. | 8. Dunfermline splint, Cowdenbeath, Pit 7. |
| 3. Ell coal, Bothwell. | 9. Boiler fuel, Aitken Pit, Kely. |
| 4. Main coal, Bothwell. | 10. Haugrigg coking coal, Kilsyth. |
| 5. Poytshaw coal, Bothwell. | 11. Coking coal, Kilsyth. |
| 6. Dunfermline splint, Cowdenbeath, Pit 10. | 12. Anthracite, Kilsyth. |

**AVERAGE PERCENTAGE COMPOSITION OF GAS WORKS TAR
(NICKELS).**

	London.	Country.
Ammoniacal liquor - -	4·5	4·0
Light oil - - - -	2·4	3·0
Carbolic and creosote oils -	20·3	22·0
Anthracene oil - - -	15·4	4·0
Pitch - - - - -	58·0	67·0

**PERCENTAGE COMPOSITION OF COAL TAR FROM HORIZONTAL
AND VERTICAL RETORTS (BUEB).**

	Horizontal Retort.	Dessau Vertical Retort.
Ammoniacal liquor - -	3·50	2·17
Light oil - - - -	3·10	5·85
Middle oil - - - -	7·68	12·32
Heavy oil - - - -	10·15	11·95
Anthracene oil - - -	11·54	15·96
Pitch - - - - -	62·00	49·75

Thermal Efficiency.

The overall thermal efficiency of an engine is the proportion which the heat converted into work bears to the total heat entering the engine.

From recent determinations of Joule's equivalent, one B.Th.U.=778 foot-pounds, from which can be calculated the value :—

$$2,545 \text{ B.Th.U.} = 1 \text{ H.P. hour.}$$

Therefore the thermal efficiency (μ) of an engine which consumes x lbs. of fuel of calorific power W for each horsepower hour is obtainable by the formula :—

$$\mu = \frac{2545}{Wx}$$

The overall thermal efficiencies of various types of engines when working under favourable conditions are roughly as follows :—

Reciprocating steam engine and boiler	-	-	12 per cent.
Steam turbine and boiler	-	-	18 „
Petrol engine (automobile)	-	-	22 „
Gas engine with producers	-	-	24 „
Gas engine with suction producer	-	-	26 „
Petrol engine (aircraft)	-	-	27 „
Semi-Diesel oil engine	-	-	28 „
Alcohol engine	-	-	36 „
Diesel oil engine	-	-	38 „

Air Required for Combustion.

The theoretical weight of air required to burn one pound of fuel can be obtained from the following equation :—

$$A = 0.116 (C + 3 [H - \frac{1}{8} O]) \text{ lbs.,}$$

where C , H , and O are the percentages of carbon, hydrogen, and oxygen respectively in the fuel.

Petrol engines closely approach the theoretical mixture, whilst heavy oil engines generally require about double the theoretical quantity of air when working at full load. Engines running on alcohol are worked most economically with the theoretical amount of air, but can be made to yield a greater power (at the expense of economy) by giving more fuel than is required by theory.

Petroleum Act, 1879—Directions for Applying the Flashing Test.

1. The test apparatus is to be placed for use in a position where it is not exposed to currents of air or draughts.

OXYGEN AND AIR REQUIRED TO BURN "N" PARTS OF
VARIOUS FUELS.

N=		1	2	3	4	5	6	7	8	9
N Kg C require	Kg. O -	2·6667	5·3333	8·0000	10·667	13·333	16·000	18·667	21·333	24·000
	Kg. Air -	11·5011	23·002	34·503	46·004	57·505	69·006	80·508	92·009	103·51
	Cb.m. O	1·8643	3·7286	5·5928	7·4571	9·3214	11·186	13·050	14·914	16·778
	Cb.m. Air	8·8944	17·789	26·683	35·578	44·172	53·367	62·261	71·156	80·050
N Kg H require	Kg. O -	7·98	15·96	23·94	25·92	39·90	47·88	55·86	63·84	71·82
	Kg. Air -	34·4170	68·834	103·25	137·67	172·08	206·50	240·92	275·34	309·75
	Cb.m. O	5·5788	11·158	16·737	23·315	27·894	33·473	39·032	44·631	50·210
	Cb.m. Air	26·5984	53·197	79·795	106·39	132·99	159·59	186·19	212·79	239·39
N Kg CO require	Kg. O -	0·5714	1·1429	1·7143	2·2857	2·8571	3·4286	4·0000	4·5714	5·1429
	Kg. Air -	2·4645	4·9291	7·3936	9·8582	12·323	14·787	17·252	19·716	22·181
	Cb.m. O	0·3995	0·7990	1·1985	1·5979	1·9974	2·3969	2·7964	3·1959	3·5954
	Cb.m. Air	1·9046	3·8093	5·7139	7·6186	9·5232	11·428	13·333	15·237	17·142
N Kg CH ₄ require	Kg. O -	3·9975	7·9950	11·992	15·900	19·987	23·985	27·982	31·980	35·978
	Kg. Air -	17·2410	34·482	51·723	68·964	86·205	103·45	120·69	137·93	155·17
	Cb.m. O	2·7947	5·5893	8·3840	11·179	13·973	16·769	19·563	22·357	25·152
	Cb.m. Air	13·3291	26·658	39·987	53·317	66·646	79·975	92·304	106·63	119·96
N Kg C ₂ H ₄ require	Kg. O -	3·4273	6·8547	10·282	13·719	17·137	20·564	23·991	27·419	30·846
	Kg. Air -	14·7820	29·564	44·346	59·128	73·910	89·692	103·47	118·26	133·04
	Cb.m. O	2·3961	4·7921	7·1882	9·5843	11·980	14·376	16·772	19·169	21·565
	Cb.m. Air	11·4280	22·856	34·284	45·712	57·140	68·568	79·996	91·424	102·86
N Cbm H require	Kg. O -	0·7174	1·4348	2·1522	2·8696	3·5870	4·3044	5·0218	5·7392	6·4566
	Kg. Air -	3·0941	7·1881	9·2822	12·376	15·470	18·564	21·658	24·752	27·847
	Cb.m. O	0·5015	1·0031	1·5046	2·0061	2·5077	3·0092	3·5107	4·0123	4·5138
	Cb.m. Air	2·3912	4·7823	7·1735	9·5647	11·956	14·347	16·738	19·129	21·521
N Cbm CO require	Kg. O -	0·7174	1·4349	2·1523	2·8697	3·5872	4·3046	5·0220	5·7394	6·4569
	Kg. Air -	3·0942	6·1885	9·2827	12·377	15·471	18·565	21·660	24·754	27·848
	Cb.m. O	0·5016	1·0031	1·5047	2·0062	2·5078	3·0094	3·5109	4·0125	4·5140
	Cb.m. Air	2·3913	4·7826	1·1739	9·5652	11·957	14·348	16·739	19·130	21·522
N Cbm CH ₄ require	Kg. O -	2·8696	5·7391	8·6087	11·478	14·348	17·217	20·087	22·957	25·826
	Kg. Air -	12·3763	24·753	37·129	49·505	61·882	74·258	86·634	99·010	111·39
	Cb.m. O	2·0061	4·0123	6·0184	8·0245	10·031	12·037	14·043	16·049	18·055
	Cb.m. Air	9·5682	19·136	28·705	38·273	47·841	57·409	66·978	76·546	86·114
N Cbm C ₂ H ₄ require	Kg. O -	4·3044	8·6087	12·913	17·217	21·522	25·826	30·131	34·435	38·739
	Kg. Air -	18·5645	37·129	55·693	74·258	92·822	111·39	129·95	148·52	167·08
	Cb.m. O	3·0092	6·0184	9·0276	12·037	15·046	18·055	21·064	24·074	27·083
	Cb.m. Air	14·3524	28·705	43·057	57·409	71·762	86·114	100·47	114·82	128·27

2. The heating vessel or water bath is filled by pouring water into the funnel until it begins to flow out at the spout of the vessel. The temperature of the water at the commencement of the test is to be 130° F., and this is attained in the first instance either by mixing hot and cold water in the bath, or in a vessel from which the bath is filled, until the thermometer which is provided for testing the temperature of the water gives the proper indication; or by heating the water by the spirit lamp (which is attached to the stand of the apparatus) until the required temperature is indicated.

If the water has been heated too highly, it is easily reduced to 130° by pouring in cold water little by little (to replace a portion of the warm water) until the thermometer gives the proper reading.

When a test has been completed, this water bath is again raised to 130° by placing the lamp underneath, and the result is readily obtained while the petroleum cup is being emptied, cooled, and refilled with a fresh sample to be tested. The lamp is then turned on its swivel from under the apparatus, and the next test is proceeded with.

3. The test-lamp is prepared for use by fitting it with a piece of flat plaited candle-wick, and filling it with colza or rape oil up to the lower edge of the opening of the spout or wick tube. The lamp is trimmed so that when lighted it gives a flame of about 0.15 of an inch diameter, and this size of flame, which is represented by the projecting white bead on the cover of the oil cup, is readily maintained by simple manipulation from time to time with a small wire trimmer.

When gas is available it may be conveniently used in place of the little oil lamp, and for this purpose a test-flame arrangement for use with gas may be substituted for the lamp.

4. The bath having been raised to the proper temperature, the oil to be tested is introduced into the petroleum cup, being poured in slowly until the level of the liquid just reaches the point of the gauge which is fixed in the cup. In warm weather the temperature of the room in which the samples to be tested have been kept should be

observed in the first instance, and if it exceeds 65° ,¹ the samples to be tested should be cooled down (to about 60°),¹ by immersing the bottles containing them in cold water, or by any other convenient method. The lid of the cup, with the slide closed, is then put on, and the cup is placed into the bath or heating vessel. The thermometer in the lid of the cup has been adjusted so as to have its bulb just immersed in the liquid, and its position is not, under any circumstances, to be altered. When the cup has been placed in the proper position, the scale of the thermometer faces the operator.

5. The test-lamp is then placed in position upon the lid of the cup, the lead-line or pendulum, which has been fixed in a convenient position in front of the operator, is set in motion, and the rise of the thermometer in the petroleum cup is watched. When the temperature has reached about 66° ,¹ the operation of testing is to be commenced, the test-flame being applied once for every rise of one degree in the following manner:—

The slide is slowly drawn open while the pendulum performs three oscillations, and is closed during the fourth oscillation.

Note.—If it is desired to employ the test apparatus to determine the flashing point of oils of very low volatility, the mode of proceeding is to be modified as follows:—

The air chamber which surrounds the cup is filled with cold water to a depth of $1\frac{1}{2}$ in., and the heating vessel or water bath is filled as usual, but also with cold water. The lamp is then placed under the apparatus, and kept there during the entire operation. If a very heavy oil is being dealt with, the operation may be commenced with water previously heated to 120° ,¹ instead of with cold water.

¹ Fahrenheit.

TEMPERATURES OF SPONTANEOUS IGNITION.¹

Description.	Specific Gravity.	Spontaneous Ignition Temp. in Oxygen.	Spontaneous Ignition Temp. in Air.
<i>Petroleum Distillates.</i>		° C.	° C.
Pratt's perfection spirit, No. 1 - - -	0·710	272	383
Petrol (Mex.) - - -	0·718	279	361
Pratt's spirit, No. 2 - - -	0·724	270	371
Taxibus spirit (A.A.O. Co. Ltd.) - - -	0·729	272	390
Paraffin oil from A.A.O. Co. - - -	0·807	251	...
Petrolite kerosene - - -	0·814	251·5	432
Empire paraffin - - -	0·782	253	395
Petrol from Anglo-American - - -	0·735	...	392
Lamp oil from Anglo-American - - -	0·787	...	367
Gas oil (A.A.O. Co. Ltd.) - - -	...	254	358
<i>Petroleum (crude and residue).</i>			
Crude petroleum (Egypt) - - -	0·851	260	...
Digboi oil (Assam) - - -	0·890	261	384
Anglo-Persian Oil Co.'s Oil - - -	0·894	254	408
Crude petroleum (Texas) - - -	0·895	256	387
Anglo-American fuel oil - - -	0·900	269	430
Anglo-Mexican oil - - -	0·908	259·5	417
Crude petroleum (Texas) - - -	0·936	268·5	416
" " (Borneo) - - -	0·939	269	380
Mexican fuel oil - - -	0·948	259·5	424
Crude petroleum (Mexico) - - -	0·949	258	425
" " (Trinidad) - - -	0·950	274	424
" " (California) - - -	0·952	264	...
Venezuelan petroleum - - -	0·955	275	429
Crude petroleum (California) - - -	0·961	262	420
<i>Shale Oils.</i>			
Oil engine oil (Broxburn Oil Co. Ltd.) - -	0·768	253	333

¹ "Spontaneous Ignition Temperatures of Liquid Fuels for Internal Combustion Engines." H. Moore, *Jour. Soc. Chem. Ind.*, 15th February 1917.

TEMPERATURES OF SPONTANEOUS IGNITION—*continued.*

Description.	Specific Gravity.	Spon- taneous Ignition Temp. in Oxygen.	Spon- taneous Ignition Temp. in Air.
<i>Shale Oils.</i>		° C.	° C.
Lighthouse oil (Broxburn Oil Co. Ltd.) -	0·803	251	322
<i>Tar Distillates.</i>			
Xylol commercial - - - - -	0·860	484	...
Toluol 90 per cent. - - - - -	0·863	516	...
Benzol 100 per cent. - - - - -	0·875	566	...
Premier tarless tar oil - - - - -	0·992	349	...
Creosote oil (Hardman & Holden) -	1·010	415	...
Water gas tar creosote (Stainsby & Lyons) -	1·036	473	...
Coke oven tar oil (Simon Carvès) - - -	1·046	478	...
<i>Tars.</i>			
Tar (product of low temp. carbonisation) -	0·987	307	508
C.W.G. tar (Stockport Gas Works) - -	1·074	464	...
Oil gas tar (Beckton) - - - - -	1·077	415	...
Horizontal retort tar (Heywood Gas Works) -	1·114	445	...
" " " (Stockport Gas Works) -	1·123	454	...
Coke oven tar (Simon Carvès) - - -	1·132	494	...
" " (Coppée Co.) - - - - -	1·140	488	...
" " (Koppers Type Ovens) - - -	1·145	495	...
Blast furnace tar (Carlton Iron Works) -	1·172	498	...
" " " (Wm. Baird & Co.) - - -	...	410	...
<i>Miscellaneous.</i>			
Alcohol - - - - -	0·817	395	518
Turpentine - - - - -	0·842	275	275
"Mirrlees-Diesel" compressor lubricating oil	0·875	265·5	405
"Mirrlees-Diesel" engine lubricating oil -	0·894	265·5	401·0
Whale oil - - - - -	0·921	273	470
Ether - - - - -	0·730	190	347
Paraffin wax - - - - -	...	245	...
Naphthalene - - - - -	...	402	...
Free carbon from tar - - - - -	...	348	...
Asphaltum from oil - - - - -	...	260	...

LOWER LIMITS FOR DOWNWARD PROPAGATION OF FLAME
IN A TUBE (AIR AND FUEL MIXTURE).

Obtained by Le Chatelier and Boudouard (Comp. Rend., 1898, 126, 1510).

	Per Cent.		Per Cent.
Hydrogen - - -	10.0	Turpentine - - -	0.73
Carbon monoxide - - -	16.0	Acetone - - -	2.9
Carbon disulphide - - -	1.94	Methyl alcohol - - -	6.0
Illuminating gas - - -	8.1	Ethyl " - - -	3.07
Methane - - -	6.0	n-Propyl " - - -	2.55
Pentane - - -	1.1	i-Propyl " - - -	2.65
Hexane - - -	1.3	i-Butyl " - - -	1.68
Heptane - - -	1.1	Allyl " - - -	3.04
Octane - - -	1.0	Amyl " - - -	1.19
Nonane - - -	0.83	Acetic acid - - -	4.05
Acetylene - - -	2.8	Ether - - -	1.9
Amylene - - -	1.6	Ethyl acetate - - -	2.3
Benzene - - -	1.5	Ethyl nitrate - - -	3.8
Toluene - - -	1.3		

LIMITS FOR DOWNWARD PROPAGATION OF FLAME
(AIR AND FUEL MIXTURE).

(As given by Eitner; obtained in a Bunte burette.)

	Lower Limit.	Upper Limit.
	Per Cent.	Per Cent.
Hydrogen - - -	9.45	66.4
Carbon monoxide - - -	16.5	74.95
Water gas - - -	12.4	66.8
Methane - - -	6.1	12.8
Ethylene - - -	4.1	14.6
Coal gas - - -	7.9	19.1
Acetylene - - -	3.45	52.2
		(75 % in large vessel)
Alcohol - - -	3.95	13.65
Ether - - -	2.75	7.7
Benzene - - -	2.65	6.5
Pentane - - -	2.4	4.9
Benzine - - -	2.4	4.9

British Admiralty Fuel Oil Specification.

1. **Quality.**—The oil fuel supplied shall consist of liquid hydrocarbons, and may be either :—

- (a) Shale oil ; or
- (b) Petroleum, as may be required ; or
- (c) A distillate or a residual product of petroleum ;
and shall comply with the Admiralty requirements as regards flash point, fluidity at low temperatures, percentage of sulphur, presence of water, acidity, and freedom from impurities.

The flash point shall not be lower than 175° F., close test—Abel or Pensky-Martens. In the case of oils of exceptionally low viscosity, such as distillates from shale, the flash point must not be less than 200° F. The proportion of sulphur contained in the oil shall not exceed 3 per cent. The oil fuel supplied shall be as free as possible from acid, and in any case the quantity of acid must not exceed .05 per cent. calculated as oleic acid when tested by shaking up the oil with distilled water, and determining by titration with decinormal alkali the amount of acid extracted by the water, methyl orange being used as indicator. The quantity of water delivered with the oil shall not exceed .5 per cent.

The viscosity of the oil supplied shall not exceed 2,000 seconds for an outflow of 50 cubic centimetres at a temperature of 32° F., as determined by Sir Boverton Redwood's standard viscometer (Admiralty type for testing oil fuel). Pending settlement of this specification, a viscosity of 1,000 seconds was provisionally adopted in 1912. The oil supplied shall be free from earthy, carbonaceous, or fibrous matter or other impurities which are likely to choke the burners. The oil shall, if required by the inspecting officer, be strained by being pumped, on discharge from the tanks or tank steamer, through filters of wire gauze having 16 meshes to the inch.

SPECIFICATION BY RATH AND ROSSENBECK, FOR THE
GERMAN TAR DISTILLERS' FEDERATION, FOR TAR
OILS FOR USE IN DIESEL ENGINES.¹

1. The tar oils must not contain more than 0·2 per cent. of solid constituents insoluble in xylol. The incombustible constituents shall not be more than 0·05 per cent.
2. The water content must not exceed 1 per cent.
3. The coke residue shall not exceed 3 per cent.
4. In the distillation test at least 60 per cent. by volume must distil over up to 300° C.
5. The net calorific power shall be not less than 8,800 cals. per kilogram.
6. The flash point must not be under 65° C.
7. The oil must flow freely at 15° C. On cooling the oil to 8° C. and allowing to rest at this temperature for half an hour, no separation shall take place.

SPECIFICATION OF THE ROUMANIAN SECTION OF THE
INTERNATIONAL COMMISSION ON PETROLEUM.

1. **Specific Gravity.**—These oils must have a specific gravity of 0·860 to 0·895 at 15° C. The gravity is to be ascertained with officially standardised hydrometers. '001 is to be added to the reading of the upper meniscus. The correction factor for specific gravity for each degree of temperature is '0007.

2. **The Flash Point**, measured by Martens-Pensky apparatus, must not be under 60° C.

3. **Distillation Test.**—100 c.c. of the oil are to be distilled as prescribed in an Engler flask. At least 90 c.c. must pass over up to 350° C., and on the distillation being continued to the coking of the residue, the weight of this residue should not exceed 0·5 gm.

4. **Reaction.**—Heavy gas oil must contain no mineral acids. For testing the same, the methyl orange test described for lamp oil is to be used.

5. **Water and Impurities.**—The oil shall be quite clear,

¹ Rath u. Rossenbeck, Glückauf, 13th May 1911.

and contain no suspended particles which can be observed by the filtration of the oil.

6. **Ash Content.**—50 gm. of oil, evaporated to dryness in a platinum dish, must leave no ponderable mass of ash behind.

7. **The Viscosity** shall be, at the highest, 2·5 Engler degrees at 20° C., and be determined by Engler's, or Engler-Ubbelohde's apparatus by the prescribed procedure.

8. **The Net Calorific Value**, determined by the Berthelot-Mahler calorimeter, shall be at least 10,000 cal.

SPECIFICATION PROPOSED BY MESSRS. MIRRLEES,
BICKERTON & DAY FOR TAR OILS FOR USE IN
DIESEL ENGINES.

1. The tar oil must be a product of the distillation of coal tar. No product which has not undergone distillation must be present.

2. Tar oil must not contain more than 0·2 per cent. of solid constituents insoluble in xylol.

3. The ash content must not be greater than 0·08 per cent.

4. The water content should not be greater than 2·5 per cent.

5. The coking residue must not exceed 3 per cent.

6. The oil must be liquid at 60° F. when maintained at that temperature for half an hour.

7. In case of crystals settling in the transport tank, the buyer to be allowed to drain off the liquid portion and return the solid to the sender.

SPECIFICATION FOR TAR OILS BY THE AUGSBURG-
NURNBERG CO.¹

The tar oil must be a distillate of coal tar.

The oil must flow freely at 61° F., and on being cooled down to 46·5° F., and resting in a place undisturbed by

¹ G. Porter, paper read before Diesel Engine Users' Association, 24th May 1917.

vibration, no separation shall take place at this temperature within the space of half an hour.

The following constituents shall not be present in quantities greater than the stated percentages:—

Ash	-	-	-	·05 per cent.
Sulphur	-	-	-	1·0 „

Proportions of water and coke residue not stated.

Per cent. insoluble in xylol, ·2 per cent.

SPECIFICATION FOR TAR OILS PROPOSED BY MR. BATHO.¹

Specific gravity	-	Between 1·0 and 1·1.
Viscosity	-	Generally 2° Engler (all coal tar oils are very fluid).
Flash point	-	100° F. to 130° F.
Colour	-	Tar oils are as a rule dark to almost black. One drop on white paper should show no black residue, as is the case with tar. This black residue means a large percentage of free carbon or other tar ingredients.
Lower calorific value	-	Between 15,800 and 16,500 B.Th.U. per 1 lb.
Ash	-	Should not exceed 1 per cent. (unburnt residue of tar oil is mostly harmless).
Water	-	Should not exceed 1 per cent.
Sulphur	-	·5 per cent. to 1 per cent.
Pitch	-	If the tar oil contains a high percentage of residue which only begins to vaporise at 400° C., then the same results can be expected as with tar; that is to say, one must anticipate a considerable amount of dirt in the engine, and the exhaust valves will require frequent cleaning and grinding in.

¹ Batho. Meeting, Diesel Engine Users' Association, 23rd February 1916.

ADMIRALTY SPECIFICATION FOR CREOSOTE
FUEL OIL

Flashpoint	-	-	Not below 175° F.
			Pensky Marten's close test.
Water	-	-	Not above 1·5 per cent.
Sulphur	-	-	„ 1·0 „

If the oil contains more than 1·5 per cent. of water but not more than 3 per cent., it shall be accepted subject to a deduction in price in proportion to the quantity of water over 1·5 per cent. therein. Deliveries containing more than 3 per cent. of water will be refused.

The fuel is required to be fluid at 90° F., and to be free from earthy carbonaceous or fibrous matter and from anthracene paste, and as free as possible from tar acids.

PETROLEUM IMPORTS OF THE UNITED KINGDOM, 1914 (QUANTITIES GIVEN IN GALLONS).¹

Country.	Illuminating.	Lubricating.	Residuals.	Gas Oil (Solar).	Benzine.	Fuel Oil.	Other Descriptions.	Totals.
Belgium -	...	538,100	2,000	...	32,230	...	1,350	573,680
Canada -	...	21,300	88,510	...	52,125,000	109,810
Dutch Indies -	90	52,125,000	83,800	1,750,240	53,958,130
Germany -	29,250	1,471,510	7,430	1,508,190
Holland -	...	12,230	...	182,000	5,063,430	280	13,690	5,271,630
Mexico -	12,364,790	256,800	2,434,380	15,031,040	995,010	31,082,020
Roumania -	13,033,080	...	961,440	...	6,412,480	2,348,570	...	22,755,570
Russia -	4,574,390	6,454,480	5,400	...	10,202,600	...	630	21,237,500
U.S.A. -	116,595,460	54,846,900	2,570,740	83,470,250	40,766,060	18,748,300	735,410	317,705,710
Other countries -	4,170	260,810	...	1,460	3,433,970	8,900	1,843,230	5,542,540
Totals -	146,601,230	63,852,130	3,628,090	83,653,710	120,460,150	36,200,890	5,346,900	459,744,780

¹ *Petroleum Review*, January 1915.

MINERAL OIL EXPORTS FROM THE UNITED STATES.¹

	Gallons.	
	1913.	1914.
Crude oil - - - - -	184,991,667	123,590,451
Illuminating oil - - - -	1,118,096,475	1,008,403,576
Lubricating and paraffin oils -	205,825,151	190,888,017
Naphthas, gasoline, etc. - -	178,971,302	199,754,004
Residuum, gas oil, fuel oil, etc. -	420,480,849	701,612,276
Total -	2,103,365,444	2,224,248,324

GLOSSARY OF TRADE NAMES FOR PETROLEUM PRODUCTS.

(From Tinkler and Challenger's "Chemistry of Petroleum.")

Albertite.—A product resembling and closely allied to asphalt.

Asphalt.—A black viscous substance often to be met with at the outcrop of petroliferous strata. Has probably been formed as a result of the evaporation and atmospheric oxidation of exuding crude petroleum. A very similar product may be obtained by blowing air through the hot residues left in petroleum stills.

Asphalt Rock.—The name applied to a stratum of sandstone or limestone when more or less saturated with asphalt.

Astatki.—See Ostatki.

Benzine.—That fraction of B.P. 70°-120° C. obtained in the refining of petroleum. Heptane, C_7H_{16} , is the principal constituent of the benzine from Pennsylvanian oil. Totally distinct from the aromatic hydrocarbon benzene, C_6H_6 .

Benzine, Heavy.—See Ligroin.

Benzoline.—The more volatile portion obtained on redistilling benzine; B.P. about 70°-95° C. Often used as synonymous with benzine.

Ceresine.—Ozokerite freed from earthy matter and purified by means of warm fuming sulphuric acid.

¹ U. S. Dept. of Commerce, January 1915.

Cymogene.—The liquid obtained by submitting the gases originally dissolved in crude petroleum to cold and pressure. B.P. 1° C. Nearly pure butane. Used in certain types of refrigerators.

Earth Wax.—See Ozokerite.

Gas, Natural.—The gaseous products arising from petroleum wells. Rich in methane and ethane.

Gasoline.—That fraction of B.P. 40° - 70° C. obtained in the refining of Pennsylvanian oil. Consists largely of pentane, C_5H_{12} , and hexane, C_6H_{14} .

Gilsonite.—A product resembling and closely allied to asphalt.

Jelly, Mineral.—See Vaseline.

Kerosene.—That fraction of B.P. 150° - 300° C. obtained on distillation of American petroleum. Kerosene contains nonane, C_9H_{20} , decane, $C_{10}H_{22}$, etc., and is used as an illuminating oil.

Ligroin.—A term rather loosely applied. Usually denotes a refined petroleum distillate of B.P. 120° - 135° C., but is occasionally applied to lower boiling fractions, such as benzoline.

Mineral Burning Oils.—Suitable for burning with a wick, *e.g.*, belmontine oil, cazeline oil, colzarine oil, mineral colza oil, mineral seal oil, mineral sperm oil, pyronaphtha (see also Kerosene).

Motor Spirit.—The saturated aliphatic hydrocarbons of American oil, the polymethylenes from Baku oil, or the unsaturated hydrocarbons from shale oil, as well as benzene, C_6H_6 , and alcohol, C_2H_5OH , are employed in internal combustion engines. The boiling points are usually below 120° C.

Naphtha.—The less volatile portion obtained on redistilling benzine. Boils from about 95° - 120° C. The term is unfortunately very loosely applied, and is synonymous with mineral naphtha. "Solvent naphtha," however, is not a petroleum product.

Green naphtha is one of the fractions obtained in the fractionation of crude shale oil.

Ostatki.—The residuum obtained in distillation of Russian petroleum. Much used as a fuel.

Ozokerite.—A peculiar wax-like substance which is forced up through the fissures of various strata. Is usually considered to have been formed by the gradual evaporation and oxidation of exuding petroleum. When purified by melting out from earthy matter, and treating with fuming sulphuric acid, is known as ceresine.

Paraffin Oil.—See Kerosene.

Paraffin Scale.—Crude paraffin wax.

Paraffin Wax.—The higher members of the series C_nH_{2n+2} , which occur in American petroleum and in shale oil, *e.g.*, $C_{24}H_{50}$. Used in the manufacture of candles.

Paraffinum Liquidum.—The medicinal petroleum of the British Pharmacopœia. Sp. gr. 0.885-0.890. B.P. above $360^{\circ}C$.

Perfumery Oil.—Refined Russian petroleum. Sp. gr. 0.880-0.885. Used in pharmacy.

Petrol.—See Light Petroleum, Benzine.

Petrolatum.—The vaseline of the United States Pharmacopœia.

Petrolatum Liquidum.—The medicinal high-boiling petroleum of the United States Pharmacopœia.

Petroleum.—Signifies the crude untreated oil.

Petroleum Ether.—See Gasoline or Benzine.

Petroleum Jelly.—See Vaseline.

Petroleum Naphtha.—Loosely employed; often denotes the first fraction (B.P. up to $150^{\circ}C$.) obtained on distillation of crude oil. Often applied to any low-boiling petroleum product.

Petroleum Spirit and Light Petroleum.—See Benzine, Benzoline, and Naphtha, with all of which the terms are more or less synonymous.

Pitch.—This term is loosely applied and may denote:—

- (i) The residue remaining in the retorts after the distillation of crude coal tar.
- (ii) A residue somewhat similar in appearance remaining after the distillation of crude petroleum.
- (iii) The asphalt of the Asphalt or Pitch Lake in Trinidad.

Polishing Oil.—That fraction of B.P. 130° - $160^{\circ}C$. obtained in refining of crude petroleum.

Reduced Oils.—High-boiling petroleum oils which have been distilled *in vacuo* and deprived of their dissolved paraffin wax by cooling and filtering through filter presses.

Residuum.—The residue obtained on the distillation of crude petroleum after the constituents boiling below 300° C. have been removed. Is worked up for paraffin wax, vaseline, and lubricating oils.

Rhigoline.—The most volatile liquid fraction obtained in the refining of crude petroleum. B.P. 18° C., used as a local anæsthetic. Consists largely of pentane, C_5H_{12} .

Shale : Oil Shale.—A highly bituminous laminated substance containing about 80 per cent. of mineral matter, occurring in many parts of the world, but especially in the coal measures of the Lothians in Scotland.

Shale Naphtha.—See Shale Spirit.

Shale Oil.—The somewhat tarry oil obtained when various bituminous shales are submitted to dry distillation. Contains unsaturated hydrocarbons and higher members of the series C_nH_{2n+2} .

Shale Spirit.—The lower boiling fractions obtained in the refining of crude shale oil. Sp. gr. 0·70-0·76. Used as a motor spirit. Contains about 50-60 per cent. of unsaturated hydrocarbons.

Sherwood Oil.—See Light Petroleum and Petroleum Ether.

Solar Oil.—High-boiling fraction of Russian petroleum used for fuel.

Solene.—See Gasoline or Petroleum Ether, with which the term is synonymous.

Vaseline.—A mixture of high-boiling solid hydrocarbons of low melting point, many of which belong to the series C_nH_{2n+2} . Sometimes contains unsaturated hydrocarbons.

Articles of the vaseline class are met with under the names ozokerine, fossiline, chrysine, cosmoline, saxoline, geoline, petrolina, vaseline tallow.

Yellow Wax.—A viscous, semi-solid, difficultly volatile substance obtained on distillation of still residuum. Contains anthracene, $C_{14}H_{10}$, and other hydrocarbons of complex structure.

CONVERSION OF DEGREES CENTIGRADE, FAHRENHEIT, AND REAMUR.

The three thermometric scales are: Celsius, or Centigrade (C.); Fahrenheit (F.); and Reamur (R.), used in Russia. The formulæ for converting one to another are:—

To convert °C. to °F.	-	-	-	$(^{\circ}\text{C.} \times \frac{9}{5}) + 32 = ^{\circ}\text{F.}$
„ °F. „ °C.	-	-	-	$(^{\circ}\text{F.} - 32) \times \frac{5}{9} = ^{\circ}\text{C.}$
„ °C. „ °R.	-	-	-	$(^{\circ}\text{C.} \times \frac{4}{5}) = ^{\circ}\text{R.}$
„ °R. „ °C.	-	-	-	$(^{\circ}\text{R.} \times \frac{5}{4}) = ^{\circ}\text{C.}$
„ °F. „ °R.	-	-	-	$(^{\circ}\text{F.} - 32) \times \frac{4}{9} = ^{\circ}\text{R.}$
„ °R. „ °F.	-	-	-	$(^{\circ}\text{R.} \times \frac{9}{4}) + 32 = ^{\circ}\text{F.}$

CONVERSION TABLE FOR DEGREES BAUMÉ (LIGHTER THAN WATER) TO SPECIFIC GRAVITY AND LBS. PER GALLON.

Degrees Baumé.	Specific Gravity.	Lbs. in 1 Gallon (American).	Degrees Baumé.	Specific Gravity.	Lbs. in 1 Gallon (American)
10	1.0000	8.33	43	.8092	6.74
11	.9929	8.27	44	.8045	6.70
12	.9859	8.21	45	.8000	6.66
13	.9790	8.16	46	.7954	6.63
14	.9722	8.10	47	.7909	6.59
15	.9655	8.04	48	.7865	6.55
16	.9589	7.99	49	.7831	6.52
17	.9523	7.93	50	.7777	6.48
18	.9459	7.88	51	.7734	6.44
19	.9395	7.83	52	.7692	6.41
20	.9333	7.78	53	.7650	6.37
21	.9271	7.72	54	.7608	6.34
22	.9210	7.67	55	.7567	6.30
23	.9150	7.62	56	.7526	6.27
24	.9090	7.57	57	.7486	6.24
25	.9032	7.53	58	.7446	6.20
26	.8974	7.48	59	.7407	6.17
27	.8917	7.43	60	.7368	6.14
28	.8860	7.38	61	.7329	6.11
29	.8805	7.34	62	.7290	6.07
30	.8750	7.29	63	.7253	6.04
31	.8695	7.24	64	.7216	6.01
32	.8641	7.20	65	.7179	5.98
33	.8588	7.15	66	.7142	5.95
34	.8536	7.11	67	.7106	5.92
35	.8484	7.07	68	.7070	5.89
36	.8433	7.03	69	.7035	5.86
37	.8383	6.98	70	.7000	5.83
38	.8333	6.94	75	.6829	5.69
39	.8284	6.90	80	.6666	5.55
40	.8235	6.86	85	.6511	5.42
41	.8187	6.82	90	.6363	5.30
42	.8139	6.78	95	.6222	5.18

The specific gravity multiplied by 10 = weight in pounds per imperial gallon.

TABLE OF CONVERSIONS OF VARIOUS MEASURES.

¹ 1 metre - - - -	= 39·370113 inches.
¹ 1 gallon - - - -	= 4·5459631 litres.
¹ 1 kilogram - - - -	= 15432·3564 grains.
1 metre - - - -	= 3·28084 feet.
„ - - - -	= 1·09361 yards.
1 foot - - - -	= ·304799 metre.
1 litre - - - -	= 61·0239 cubic inches.
„ - - - -	= ·219975 gallon.
1 cubic metre - - - -	= 35·3147 cubic feet.
„ „ - - - -	= 1·30975 cubic yards.
„ foot - - - -	= 28·3167 litres.
1 kilogram - - - -	= 2·20462 pounds.
1 pound - - - -	= ·453592 kilogram.
1 metric ton - - - -	= 1,000 kilograms.
„ „ - - - -	= ·984206 ton English.
„ „ - - - -	= 2204·62 pounds.
1 ton English - - - -	= 1016·04 kilograms.
„ „ - - - -	= 1·01604 metric tons.
1 gram per square millimetre	= 1·42233 pounds per square inch.
„ „ centimetre	= ·014223 „ „ „ „
1 pound per square inch -	= ·703071 grams per square millimetre.
„ „ „ -	= 5·17006 centimetres mercury.
1 atmosphere - - - -	= 14·7 pounds per square inch.
„ - - - -	= 1·03351 kilograms per square centimetre
1 British thermal unit -	= 778 foot-pounds.
1 foot-pound - - - -	= ·138254 kilogrammetre.
1 kilogrammetre - - - -	= 7·23301 foot-pounds.
1 British thermal unit -	= 107·562 kilogrammetres.
1 large calorie (k) - -	= 1,000 small calories (c).
1 British thermal unit -	= ·251995 calorie (k).
1 calorie (k) - - - -	= 426·841 kilogrammetres.
„ - - - -	= 3087·35 foot-pounds.
1 horse power - - - -	= 33,000 foot-pounds per minute.
„ - - - -	= 550 foot-pounds per second.
1 force de cheval - - -	= 75 kilogrammetres per second.
1 cheval - - - -	= ·986319 horse power.
1 horse power - - - -	= 1·01387 chevaux.
1 pound per horse power -	= ·447386 kilogram per cheval.
1 kilogram per cheval -	= 2·23520 pounds per horse power.
1 cubic foot per horse power -	= ·027929 cubic metre per cheval.
1 square „ „ „ -	= ·091631 square „ „ „
1 „ metre per cheval -	= 10·9132 „ feet per horse power.
1 cubic „ „ „ -	= 35·8045 cubic „ „ „
1 B.Th. U. per square foot -	= 2·71246 calories per square metre.

¹ Legalised fundamental equivalents.

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